

09/856017

IMPROVED UNCOMPLEXED CYCLODEXTRIN COMPOSITIONS
FOR ODOR CONTROL

5

10

TECHNICAL FIELD

The present invention relates to stable, preferably clear, aqueous odor-absorbing compositions, articles of manufacture, and/or method of use, comprising solubilized, uncomplexed cyclodextrin, and perfume in cyclodextrin compatible form. As used herein, "cyclodextrin compatible" means that the cyclodextrin and the perfume, do not substantially interact so as to eliminate the odor controlling ability of the cyclodextrin or the desired effect of the perfume. The odor-absorbing composition is designed to control odors caused by a broad spectrum of organic odoriferous materials, which may, or may not, contain reactive functional groups, and to preferably remain shelf stable for a substantial period of time. Preferably, the aqueous odor-absorbing compositions are for use on inanimate surfaces, especially fabrics, and more specifically, clothes, in order to restore and/or maintain freshness by reducing malodor without the need for washing or dry cleaning.

25

BACKGROUND OF THE INVENTION

The present invention relates to stable, preferably clear, aqueous odor absorbing compositions, articles of manufacture and/or method for use, especially on inanimate surfaces, i.e., other than directly on human skin, as an odor-absorbing composition. Such compositions preferably provide a "scent signal" in the form of a pleasant odor which signals the removal of the malodor. Preferably, the compositions are sprayed onto fabrics, particularly clothes, to restore their freshness by reducing malodor without washing or dry

30

09/856017 "051601"

cleaning. The aqueous odor-absorbing compositions are also preferably for use on other inanimate surfaces, such as household upholsteries, drapes, carpets, car interiors, and the like. They also can be used on, e.g., human and animal surfaces, e.g., skin, hair, etc.

Uncomplexed cyclodextrin molecules, which are made up of varying numbers of glucose units provide the absorbing advantages of known absorbent deodorizing compositions without harmful effects to fabrics. While cyclodextrin is an effective odor absorbing active, some small molecules are not sufficiently absorbed by the cyclodextrin molecules because the cavity of the cyclodextrin molecule may be too large to adequately hold the smaller organic molecule. If a small sized organic odor molecule is not sufficiently absorbed into the cyclodextrin cavity, a substantial amount of malodor can remain. In order to alleviate this problem, low molecular weight polyols can be added to the composition to enhance the formation of cyclodextrin inclusion complexes. Furthermore, optional water soluble metal salts can be added to complex with some nitrogen-containing and sulfur-containing malodor molecules.

Since cyclodextrin is a prime breeding ground for certain microorganisms, especially when in aqueous compositions, it is preferable to include a water-soluble antimicrobial preservative, which is effective for inhibiting and/or regulating microbial growth, to increase storage stability of clear, aqueous odor-absorbing solutions containing water-soluble cyclodextrin, when the composition does not contain an antimicrobial material as described hereinafter.

It is also desirable to provide optional ingredients such as a cyclodextrin compatible antimicrobial active that provides substantial kill of organisms that cause, e.g., odor, infections, etc. It is also desirable that the compositions contain a cyclodextrin compatible surfactant to promote spreading of the odor absorbing composition on hydrophobic surfaces such as polyester, nylon, etc. as well as to penetrate any oily, hydrophobic soil for improved malodor control. Furthermore, it is desirable that the cyclodextrin-compatible surfactant provide in-wear electrostatic control. It is more preferable that the odor absorbing composition of the present invention contain both a cyclodextrin-compatible antibacterial active and a cyclodextrin-compatible surfactant. A cyclodextrin-compatible active is one which does not substantially form a complex with cyclodextrin in the composition, at the usage concentration, so that an effective amount of

both the free, uncomplexed active and free, uncomplexed cyclodextrin are available for their intended uses. Furthermore, it is desirable to include a humectant to maintain a desirable moisture level in cotton fabrics while they dry to maximize dewrinkling.

SUMMARY OF THE INVENTION

5 The present invention relates to a stable, preferably clear, aqueous odor-absorbing composition, preferably for use on inanimate surfaces, comprising:

10 (A). an effective amount to absorb malodors, typically from about 0.01% to about 20% by weight of the composition, with concentrated compositions which are meant to be diluted containing from about 3% to about 20%, preferably from about 5% to about 10% by weight of the composition, and, for more dilute "usage conditions" compositions, a range of from about 0.01% to about 5%, preferably from about 0.1% to about 3%, more preferably from about 0.5% to about 2%, by weight of the usage composition, of solubilized, uncomplexed cyclodextrin;

15 (B). an effective amount to improve acceptance of the composition, typically from about 0.003% to about 0.5%, preferably from about 0.01% to about 0.3%, more preferably from about 0.05% to about 0.2%, by weight of the usage composition of an emulsion or dispersion comprising perfume, containing at least about 50%, preferably at least about 60%, more preferably at least about 70%, and yet more preferably at least about 80%, by weight of the perfume of perfume ingredients that have a ClogP of more than about 3, preferably more than about 3.5 and a molecular weight of more than about 210, preferably more than about 220, the particle size of said emulsion or dispersion being large enough that it cannot be complexed by said cyclodextrin;

20 (C). optionally, but preferably, an effective amount to improve the performance of the composition, preferably from about 0.01% to about 2%, more preferably from about 0.03% to about 0.6%, and even more preferably from about 0.05% to about 0.3%, by weight of the usage composition, of cyclodextrin compatible surfactant that preferably provides a surface tension of from about 20 dyne/cm to about 60 dyne/cm, preferably from

25

30

about 20 dyne/cm to about 45 dyne/cm (with concentrated compositions having a level of from about 0.1% to about 8%, preferably from about 0.2% to about 4%, more preferably from about 0.3% to about 3%, by weight of the concentrated solution, of cyclodextrin-compatible surfactant);

- (D). optionally, an effective amount, to kill, or reduce the growth of microbes, of cyclodextrin compatible and water soluble antimicrobial active, preferably from about 0.001% to about 0.8%, more preferably from about 0.002% to about 0.3%, even more preferably from about 0.003% to about 0.2%, by weight of the usage composition, and preferably selected from the group consisting of halogenated compounds, cyclic nitrogen compounds, quaternary compounds, and phenolic compounds (with concentrated compositions having a level of from about 0.003% to about 2%, preferably from about 0.01% to about 1.2%, more preferably from about 0.1% to about 0.8%, by weight of the concentrated solution, of cyclodextrin-compatible and water soluble antimicrobial active);
- (E). optionally, but preferably, from about 0.01% to about 3%, more preferably from about 0.05% to about 1%, and even more preferably from about 0.1% to about 0.5%, by weight of the usage composition of low molecular weight polyol;
- (F). optionally, from about 0.001% to about 0.3%, preferably from about 0.01% to about 0.1%, more preferably from about 0.02% to about 0.05%, by weight of the usage composition of aminocarboxylate chelator;
- (G). optionally, but preferably, an effective amount of metallic salt, preferably from about 0.1% to about 10%, more preferably from about 0.2% to about 8%, even more preferably from about 0.3% to about 5% by weight of the usage composition, especially water soluble copper and/or zinc salts, for improved odor benefit;
- (H). optionally, an effective amount of enzyme, from about 0.0001% to about 0.5%, preferably from about 0.001% to about 0.3%, more preferably from

about 0.005% to about 0.2% by weight of the usage composition, for improved odor control benefit;

(I). optionally, an effective amount of solubilized, water-soluble, antimicrobial preservative, preferably from about 0.0001% to about 0.5%, more preferably from about 0.0002% to about 0.2%, most preferably from about 0.0003% to about 0.1%, by weight of the composition;

(J). optionally, but preferably, an effective amount of water soluble anionic polymer, e.g. polyacrylic acids or their water soluble salts, at a level of from about 0.001% to about 3%, preferably from about 0.005% to about 2%, more preferably from about 0.01% to about 1% by weight of the composition, for improved odor control benefit; and

(K). aqueous carrier that optionally can contain up to 5% of a lower molecular weight, water soluble alcohol,

said composition preferably being essentially free of any material that would soil or stain fabric under usage conditions, and/or preferably having a pH of more than about 3, more preferably more than about 3.5.

The present invention also relates to concentrated compositions, wherein the level of cyclodextrin is from about 3% to about 20%, more preferably from about 5% to about 10%, by weight of the composition which are diluted to form compositions with the usage concentrations of cyclodextrin of, e.g., from about 0.1% to about 5%, by weight of the diluted composition, as given hereinabove, which are to the "usage conditions".

The present invention also relates to the compositions incorporated into a spray dispenser to create an article of manufacture that can facilitate treatment of articles and/or surfaces with said compositions containing uncomplexed cyclodextrin and other optional ingredients at a level that is effective, yet is not discernible when dried on the surfaces.

The present invention also comprises the use of the compositions herein to treat surfaces, especially fabrics, to provide superior perfume effects.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a stable, preferably clear, aqueous odor-absorbing composition, preferably for use on inanimate surfaces, comprising:

- (A). an effective amount to absorb malodors, typically from about 0.01% to about 20% by weight of the composition, with concentrated compositions which are meant to be diluted containing from about 3% to about 20%, preferably from about 5% to about 10% by weight of the composition, and, for more dilute "usage conditions" compositions, a range of from about 0.01% to about 5%, preferably from about 0.1% to about 3%, more preferably from about 0.5% to about 2%, by weight of the usage composition, of solubilized, uncomplexed cyclodextrin;
- (B). an effective amount to improve acceptance of the composition, typically from about 0.003% to about 0.5%, preferably from about 0.01% to about 0.3%, more preferably from about 0.05% to about 0.2%, by weight of the usage composition of an emulsion or dispersion comprising perfume, containing at least about 50%, preferably at least about 60%, more preferably at least about 60%, even more preferably at least about 70%, and yet more preferably at least about 80%, by weight of the perfume of perfume ingredients that have a ClogP of more than about 3, preferably more than about 3.5, and a molecular weight of more than about 210, preferably more than about 220, the particle size of said emulsion or dispersion being large enough that it cannot be complexed by said cyclodextrin;
- (C). optionally, an effective amount to improve the performance of the composition, preferably from about 0.01% to about 2%, more preferably from about 0.03% to about 0.6%, and even more preferably from about 0.05% to about 0.3%, by weight of the usage composition, of cyclodextrin compatible surfactant that preferably provides a surface tension of from about 20 dyne/cm to about 60 dyne/cm, preferably from about 20 dyne/cm to about 45 dyne/cm (with concentrated compositions having a level of from about 0.1% to about 8%, preferably from about 0.2% to about 4%, more preferably from about 0.3% to about 3%, by weight of the concentrated solution, of cyclodextrin-compatible surfactant);

- (D). optionally, an effective amount, to kill, or reduce the growth of microbes, of cyclodextrin compatible and water soluble antimicrobial active, preferably from about 0.001% to about 0.8%, more preferably from about 0.002% to about 0.3%, even more preferably from about 0.003% to about 0.2%, by weight of the usage composition, and preferably selected from the group consisting of halogenated compounds, cyclic nitrogen compounds, quaternary compounds, and phenolic compounds (with concentrated compositions having a level of from about 0.003% to about 2%, preferably from about 0.01% to about 1.2%, more preferably from about 0.1% to about 0.8%, by weight of the concentrated solution, of cyclodextrin-compatible and water soluble antimicrobial active);
- (E). optionally, but preferably, from about 0.01% to about 3%, more preferably from about 0.05% to about 1%, and even more preferably from about 0.1% to about 0.5%, by weight of the usage composition of low molecular weight polyol;
- (F). optionally, from about 0.001% to about 0.3%, preferably from about 0.01% to about 0.1%, more preferably from about 0.02% to about 0.05%, by weight of the usage composition of aminocarboxylate chelator;
- (G). optionally, but preferably, an effective amount of metallic salt, preferably from about 0.1% to about 10%, more preferably from about 0.2% to about 8%, even more preferably from about 0.3% to about 5% by weight of the usage composition, especially water soluble copper and/or zinc salts, for improved odor benefit;
- (H). optionally, an effective amount of enzyme, from about 0.0001% to about 0.5%, preferably from about 0.001% to about 0.3%, more preferably from about 0.005% to about 0.2% by weight of the usage composition, for improved odor control benefit;
- (I). optionally, an effective amount of solubilized, water-soluble, antimicrobial preservative, preferably from about 0.0001% to about 0.5%, more preferably from about 0.0002% to about 0.2%, most preferably from about 0.0003% to about 0.1%, by weight of the composition;

- (J) optionally, but preferably, an effective amount of water soluble anionic polymer, e.g. polyacrylic acids and their water soluble salts, from about 0.001% to about 3%, preferably from about 0.005% to about 2%, more preferably from about 0.01% to about 1% by weight of the composition.
- 5 for improved odor control benefit; and
- (K). the balance being aqueous carrier that optionally can contain up to about 5% lower molecular weight water soluble alcohol,

said composition preferably being essentially free of any material that would soil or stain fabric under usage conditions, and/or preferably having a pH of more than about 3, more preferably more than about 3.5.

The present invention also relates to concentrated compositions, wherein the level of cyclodextrin is from about 3% to about 20%, preferably from about 4% to about 15%; more preferably from about 5% to about 10%, by weight of the concentrated composition. The concentrated composition is typically diluted to form usage compositions, with the usage concentration of, e.g., from about 0.1% to about 5%, by weight of the usage composition, as given hereinabove. Specific levels of other optional ingredients in the concentrated composition can readily be determined from the desired usage composition and the desired degree of concentration.

Interestingly, the longer lasting scent benefit from the selected group of perfume ingredients, defined by (B), can also be recognized without the use of cyclodextrin or cyclodextrin derivatives.

I. COMPOSITION

(A). CYCLODEXTRIN

As used herein, the term "cyclodextrin" includes any of the known cyclodextrins such as unsubstituted cyclodextrins containing from six to twelve glucose units, especially, alpha-cyclodextrin, beta-cyclodextrin, gamma-cyclodextrin and/or their derivatives and/or mixtures thereof. The alpha-cyclodextrin consists of six glucose units, the beta-cyclodextrin consists of seven glucose units, and the gamma-cyclodextrin consists of eight glucose units arranged in donut-shaped rings. The specific coupling and conformation of the glucose units give the cyclodextrins a rigid, conical molecular structures with hollow interiors of specific volumes. The "lining" of each internal cavity

is formed by hydrogen atoms and glycosidic bridging oxygen atoms; therefore, this surface is fairly hydrophobic. The unique shape and physical-chemical properties of the cavity enable the cyclodextrin molecules to absorb (form inclusion complexes with) organic molecules or parts of organic molecules which can fit into the cavity. Many
5 odorous molecules can fit into the cavity including many malodorous molecules and perfume molecules. Therefore, cyclodextrins, and especially mixtures of cyclodextrins with different size cavities, can be used to control odors caused by a broad spectrum of organic odoriferous materials, which may, or may not, contain reactive functional groups. The complexation between cyclodextrin and odorous molecules occurs rapidly in the
10 presence of water. However, the extent of the complex formation also depends on the polarity of the absorbed molecules. In an aqueous solution, strongly hydrophilic molecules (those which are highly water-soluble) are only partially absorbed, if at all. Therefore, cyclodextrin does not complex effectively with some very low molecular weight organic amines and acids when they are present at low levels on wet fabrics. As
15 the water is being removed however, e.g., the fabric is being dried off, some low molecular weight organic amines and acids have more affinity and will complex with the cyclodextrins more readily.

The cavities within the cyclodextrin in the solution of the present invention should remain essentially unfilled (the cyclodextrin remains uncomplexed) while in solution, in
20 order to allow the cyclodextrin to absorb various odor molecules when the solution is applied to a surface. Non-derivatised (normal) beta-cyclodextrin can be present at a level up to its solubility limit of about 1.85% (about 1.85g in 100 grams of water) at room temperature. Beta-cyclodextrin is not preferred in compositions which call for a level of cyclodextrin higher than its water solubility limit. Non-derivatised beta-cyclodextrin is
25 generally not preferred when the composition contains surfactant since it affects the surface activity of most of the preferred surfactants that are compatible with the derivatized cyclodextrins.

Preferably, the odor absorbing solution of the present invention is clear. The term "clear" as defined herein means transparent or translucent, preferably transparent, as in
30 "water clear," when observed through a layer having a thickness of less than about 10 cm.

Preferably, the cyclodextrins used in the present invention are highly water-soluble such as, alpha-cyclodextrin and/or derivatives thereof, gamma-cyclodextrin and/or derivatives thereof, derivatised beta-cyclodextrins, and/or mixtures thereof. The derivatives of cyclodextrin consist mainly of molecules wherein some of the OH groups are converted to OR groups. Cyclodextrin derivatives include, e.g., those with short chain alkyl groups such as methylated cyclodextrins, and ethylated cyclodextrins, wherein R is a methyl or an ethyl group; those with hydroxyalkyl substituted groups, such as hydroxypropyl cyclodextrins and/or hydroxyethyl cyclodextrins, wherein R is a -CH₂-CH(OH)-CH₃ or a -CH₂CH₂-OH group; branched cyclodextrins such as maltose-bonded cyclodextrins; cationic cyclodextrins such as those containing 2-hydroxy-3-(dimethylamino)propyl ether, wherein R is CH₂-CH(OH)-CH₂-N(CH₃)₂ which is cationic at low pH; quaternary ammonium, e.g., 2-hydroxy-3-(trimethylammonio)propyl ether chloride groups, wherein R is CH₂-CH(OH)-CH₂-N⁺(CH₃)₃Cl⁻; anionic cyclodextrins such as carboxymethyl cyclodextrins, cyclodextrin sulfates, and cyclodextrin succinylates; amphoteric cyclodextrins such as carboxymethyl/quaternary ammonium cyclodextrins; cyclodextrins wherein at least one glucopyranose unit has a 3-6-anhydro-cyclomalto structure, e.g., the mono-3-6-anhydrocyclodextrins, as disclosed in "Optimal Performances with Minimal Chemical Modification of Cyclodextrins", F. Diedaini-Pilard and B. Perly, The 7th International Cyclodextrin Symposium Abstracts, April 1994, p. 49, said references being incorporated herein by reference; and mixtures thereof. Other cyclodextrin derivatives are disclosed in U.S. Pat. Nos: 3,426,011, Parmerter et al., issued Feb. 4, 1969; 3,453,257; 3,453,258; 3,453,259; and 3,453,260, all in the names of Parmerter et al., and all issued July 1, 1969; 3,459,731, Gramera et al., issued Aug. 5, 1969; 3,553,191, Parmerter et al., issued Jan. 5, 1971; 3,565,887, Parmerter et al., issued Feb. 23, 1971; 4,535,152, Szejtli et al., issued Aug. 13, 1985; 4,616,008, Hirai et al., issued Oct. 7, 1986; 4,678,598, Ogino et al., issued Jul. 7, 1987; 4,638,058, Brandt et al., issued Jan. 20, 1987; and 4,746,734, Tsuchiyama et al., issued May 24, 1988; all of said patents being incorporated herein by reference.

Highly water-soluble cyclodextrins are those having water solubility of at least about 10 g in 100 ml of water at room temperature, preferably at least about 20 g in 100

ml of water, more preferably at least about 25 g in 100 ml of water at room temperature. The availability of solubilized, uncomplexed cyclodextrins is essential for effective and efficient odor control performance. Solubilized, water-soluble cyclodextrin can exhibit more efficient odor control performance than non-water-soluble cyclodextrin when deposited onto surfaces, especially fabric.

Examples of preferred water-soluble cyclodextrin derivatives suitable for use herein are hydroxypropyl alpha-cyclodextrin, methylated alpha-cyclodextrin, methylated beta-cyclodextrin, hydroxyethyl beta-cyclodextrin, and hydroxypropyl beta-cyclodextrin. Hydroxyalkyl cyclodextrin derivatives preferably have a degree of substitution of from about 1 to about 14, more preferably from about 1.5 to about 7, wherein the total number of OR groups per cyclodextrin is defined as the degree of substitution. Methylated cyclodextrin derivatives typically have a degree of substitution of from about 1 to about 18, preferably from about 3 to about 16. A known methylated beta-cyclodextrin is heptakis-2,6-di-O-methyl- β -cyclodextrin, commonly known as DIMEB, in which each glucose unit has about 2 methyl groups with a degree of substitution of about 14. A preferred, more commercially available, methylated beta-cyclodextrin is a randomly methylated beta-cyclodextrin, commonly known as RAMEB, having different degrees of substitution, normally of about 12.6. RAMEB is more preferred than DIMEB, since DIMEB affects the surface activity of the preferred surfactants more than RAMEB. The preferred cyclodextrins are available, e.g., from Cerestar USA, Inc. and Wacker Chemicals (USA), Inc.

It is also preferable to use a mixture of cyclodextrins. Such mixtures absorb odors more broadly by complexing with a wider range of odoriferous molecules having a wider range of molecular sizes. Preferably at least a portion of the cyclodextrins is alpha-cyclodextrin and its derivatives thereof, gamma-cyclodextrin and its derivatives thereof, and/or derivatised beta-cyclodextrin, more preferably a mixture of alpha-cyclodextrin, or an alpha-cyclodextrin derivative, and derivatised beta-cyclodextrin, even more preferably a mixture of derivatised alpha-cyclodextrin and derivatised beta-cyclodextrin, most preferably a mixture of hydroxypropyl alpha-cyclodextrin and hydroxypropyl beta-cyclodextrin, and/or a mixture of methylated alpha-cyclodextrin and methylated beta-cyclodextrin.

For controlling odor on fabrics, the composition is preferably used as a spray. It is preferable that the usage compositions of the present invention contain low levels of cyclodextrin so that a visible stain does not appear on the fabric at normal usage levels. Preferably, the solution used to treat the surface under usage conditions is virtually not discernible when dry. Typical levels of cyclodextrin in usage compositions for usage conditions are from about 0.01% to about 5%, preferably from about 0.1% to about 4%, more preferably from about 0.5% to about 2% by weight of the composition. Compositions with higher concentrations can leave unacceptable visible stains on fabrics as the solution evaporates off of the fabric. This is especially a problem on thin, colored, synthetic fabrics. In order to avoid or minimize the occurrence of fabric staining, it is preferable that the fabric be treated at a level of less than about 5 mg of cyclodextrin per gram of fabric, more preferably less than about 2 mg of cyclodextrin per gram of fabric. The presence of the surfactant can improve appearance by minimizing localized spotting.

Concentrated compositions can also be used in order to deliver a less expensive product. When a concentrated product is used, i.e., when the level of cyclodextrin used is from about 3% to about 20%, more preferably from about 5% to about 10%, by weight of the concentrated composition, it is preferable to dilute the concentrated composition before treating fabrics in order to avoid staining. Preferably the concentrated cyclodextrin composition is diluted with about 50% to about 6000%, more preferably with about 75% to about 2000%, most preferably with about 100% to about 1000% by weight of the concentrated composition of water. The resulting diluted compositions have usage concentrations of cyclodextrin as discussed hereinbefore, e.g., of from about 0.1% to about 5%, by weight of the diluted composition.

(B). PERFUME

The odor absorbing composition of the present invention provides a "scent signal" in the form of a pleasant odor which signals the removal of malodor from fabrics. The perfume herein is designed to provide, at least in part, a lasting perfume scent. Perfume is added at levels of from about 0% to about 0.5%, preferably from about 0.003% to about 0.3%, more preferably from about 0.005% to about 0.2%, by weight of the usage composition.

Perfume is added to provide a more lasting odor on surfaces. When stronger levels of perfume are preferred, relatively higher levels of perfume can be added. Any type of perfume can be incorporated into the composition of the present invention so long as the preferred hydrophobic perfume that will complex with the cyclodextrin is formed into an emulsion with a droplet size that will not readily interact with the cyclodextrin in the composition. The perfume ingredients can be either hydrophilic or hydrophobic.

If the perfume ingredients are hydrophilic, they should be dissolved in the aqueous phase so they do not complex with the cyclodextrin. It is important to note that for best product stability and improved cyclodextrin compatibility, a clear premix consisting of hydrophilic perfume ingredients, cyclodextrin compatible surfactant, and solubility aid (for example, ethanol) is firstly made so that all hydrophilic perfume ingredients are pre-dissolved. Cyclodextrin, water hold and optional ingredients are always added during the final mixing stage. In order to reserve an effective amount of cyclodextrin molecules for odor control, hydrophilic perfume ingredients are typically present at a level wherein less than about 90% of the cyclodextrin complexes with the perfume, preferably less than about 50% of the cyclodextrin complexes with the perfume, more preferably, less than about 30% of the cyclodextrin complexes with the perfume, and most preferably, less than about 10% of the cyclodextrin complexes with the perfume. The cyclodextrin to perfume weight ratio should be greater than about 8:1, preferably greater than about 10:1, more preferably greater than about 20:1, even more preferably greater than 40:1 and most preferably greater than about 70:1.

Hydrophilic perfumes are composed predominantly of ingredients having a ClogP of less than about 3.5, more preferably less than about 3.0.

(a). Hydrophobic Perfume Ingredients

In order to provide long lasting effects, the perfume is at least partially hydrophobic and has a relatively high boiling point. I.e., it is composed predominantly of ingredients selected from two groups of ingredients, namely, (a) hydrophilic ingredients having a ClogP of more than about 3, more preferably more than about 3.5, and (b) ingredients having a molecular weight above about 210, preferably above about 220. Typically, at least about 50%, preferably at least about 60%, more preferably at least about 70%, and most preferably at least about 80% by weight of the perfume is composed

of perfume ingredients of the above groups (a) and (b). For these preferred perfumes, the cyclodextrin to perfume weight ratio is typically of from about 2:1 to about 200:1; preferably from about 4:1 to about 100:1, more preferably from about 6:1 to about 50:1, and even more preferably from about 8:1 to about 30:1.

5 Hydrophobic perfume ingredients have a tendency to complex with the cyclodextrins. The degree of hydrophobicity of a perfume ingredient can be correlated with its octanol/water partition coefficient P . The octanol/water partition coefficient of a perfume ingredient is the ratio between its equilibrium concentration in octanol and in water. A perfume ingredient with a greater partition coefficient P is considered to be
10 more hydrophobic. Conversely, a perfume ingredient with a smaller partition coefficient P is considered to be more hydrophilic. Since the partition coefficients of the perfume ingredients normally have high values, they are more conveniently given in the form of their logarithm to the base 10, $\log P$. Thus the preferred perfume hydrophobic perfume ingredients of this invention have $\log P$ of about 3 or higher, preferably of about 3.5 or
15 higher.

The $\log P$ of many perfume ingredients have been reported; for example, the Pomona92 database, available from Daylight Chemical Information Systems, Inc. (Daylight CIS), Irvine, California, contains many, along with citations to the original literature. However, the $\log P$ values are most conveniently calculated by the "CLOGP"
20 program, also available from Daylight CIS. This program also lists experimental $\log P$ values when they are available in the Pomona92 database. The "calculated $\log P$ " (ClogP) is determined by the fragment approach of Hansch and Leo (cf., A. Leo, in Comprehensive Medicinal Chemistry, Vol. 4, C. Hansch, P. G. Sammens, J. B. Taylor and C. A. Ramsden, Eds., p. 295, Pergamon Press, 1990, incorporated herein by
25 reference). The fragment approach is based on the chemical structure of each perfume ingredient, and takes into account the numbers and types of atoms, the atom connectivity, and chemical bonding. The ClogP values, which are the most reliable and widely used estimates for this physicochemical property, are used instead of the experimental $\log P$ values in the selection of perfume ingredients which are useful in the present invention.

30 Non-limiting examples of the more preferred hydrophobic (enduring) perfume ingredients are selected from the group consisting of: diethyl phthalate, methyl dihydro

09356017-051601

jasmonate, lylal, hexyl salicylate, iso-E super, hexyl cinnamic aldehyde, iso-propyl myristate, galaxolide, phenyl-ethyl-phenyl acetate, cis-jasmone; dimethyl benzyl carbinyl acetate; ethyl vanillin; geranyl acetate; alpha-ionone; beta-ionone; gamma-ionone; lauric aldehyde; methyl dihydrojasmonate; methyl nonyl acetaldehyde; gamma-nonolactone; phenoxy ethyl iso-butyrate; phenyl ethyl dimethyl carbinol; phenyl ethyl dimethyl carbinyl acetate; alpha-methyl-4-(2-methylpropyl)-benzenepropanal (Suzaral T); 6-acetyl-1,1,3,4,4,6-hexamethyl tetrahydronaphthalene (Tonalid); undecylenic aldehyde; vanillin; 2,5,5-trimethyl-2-pentyl-cyclopentanone (veloutone); 2-tert-butylcyclohexanol (verdol); verdox; para-tert-butylcyclohexyl acetate (vertenex); and mixtures thereof. Enduring perfume compositions can be formulated using these enduring perfume ingredients, preferably at a level of at least about 5%, more preferably at least about 10%, and even more preferably at least about 20%, by weight of the enduring perfume composition, the total level of enduring perfume ingredients, as disclosed herein, being at least about 70%, all by weight of said enduring perfume composition.

Other enduring perfume ingredients that can be used with the above named enduring perfume ingredients can be characterized by boiling point (B.P.) and octanol/water partitioning coefficient (P). The octanol/water partitioning coefficient of a perfume ingredient is the ratio between its equilibrium concentrations in octanol and in water. These other enduring perfume ingredients of this invention have a molecular weight of more than about 210, preferably more than about 220; and an octanol/water partitioning coefficient P of about 1,000 or higher. Since the partitioning coefficients of these other enduring perfume ingredients of this invention have high values, they are more conveniently given in the form of their logarithm to the base 10, logP. Thus these other enduring perfume ingredients of this invention have logP of about 3 or higher, preferably more than about 3.1, and even more preferably more than about 3.2.

The following table illustrates the molecular weight property of some of the preferred perfume versus non-preferred perfume components.

Examples of Perfume Components
for CD Interaction

Perfume component	Molecular weight	CD interaction
Diethyl Phthalate	222.0	weak
Methyl Dihydro Jasmonate	226.3	weak
Lylal	210.3	weak
Hexyl Salicylate	222.3	weak
Iso-E Super	234.0	weak
Hexyl cinnamic Aldehyde	216.3	weak
Iso-propyl Myristate	270.0	weak
Galaxolide	258	weak
Tonalid	258	weak
Phenyl-Ethyl-Phenyl Acetate	240	weak
Tetrahydrolinalol	158.0	significant
Koavone	182.0	strong
Terpinyl Acetate	196.0	significant
Vertenex	198.3	strong
Flor Acetate	192.0	strong
a-ionone	192.3	strong
Cymal	170.0	strong
a-Me Ionone	206.3	strong
Frutene	206.0	strong
Lilial	204.3	strong

Nonlimiting examples of other preferred hydrophobic perfume ingredients which can be used in perfume compositions of this invention are:

Examples of Other Enduring Perfume Ingredients

		Approximate	
<u>Perfume Ingredients</u>		<u>B.P. (°C) (a)</u>	<u>ClogP</u>
5	BP \geq 250°C and ClogP \geq 3.0		
	Allyl cyclohexane propionate	267	3.935
	Ambrettolide	300	6.261
	Ambrox DL (Dodecahydro-3a,6,6,9a-		
10	tetramethyl-naphtho[2,1-b]furan)	250	5.400
	Amyl benzoate	262	3.417
	Amyl cinnamate	310	3.771
	Amyl cinnamic aldehyde	285	4.324
	Amyl cinnamic aldehyde dimethyl acetal	300	4.033
15	iso-Amyl salicylate	277	4.601
	Aurantiol	450	4.216
	Benzophenone	306	3.120
	Benzyl salicylate	300	4.383
	para-tert-Butyl cyclohexyl acetate	+250	4.019
20	iso-Butyl quinoline	252	4.193
	beta-Caryophyllene	256	6.333
	Cadinene	275	7.346
	Cedrol	291	4.530
	Cedryl acetate	303	5.436
25	Cedryl formate	+250	5.070
	Cinnamyl cinnamate	370	5.480
	Cyclohexyl salicylate	304	5.265
	Cyclamen aldehyde	270	3.680
	Dihydro isojasmonate	+300	3.009
30	Diphenyl methane	262	4.059
	Diphenyl oxide	252	4.240

09856017-051601

	Dodecalactone	258	4.359
	iso E super	+250	3.455
	Ethylene brassylate	332	4.554
	Ethyl methyl phenyl glycidate	260	3.165
5	Ethyl undecylenate	264	4.888
	Exaltolide	280	5.346
	Galaxolide	+250	5.482
	Geranyl anthranilate	312	4.216
	Geranyl phenyl acetate	+250	5.233
10	Hexadecanolide	294	6.805
	Hexenyl salicylate	271	4.716
	Hexyl cinnamic aldehyde	305	5.473
	Hexyl salicylate	290	5.260
	alpha-Irone	250	3.820
15	Lilial (p-t-bucinal)	258	3.858
	Linalyl benzoate	263	5.233
	2-Methoxy naphthalene	274	3.235
	gamma-n-Methyl ionone	252	4.309
	Musk indanone	+250	5.458
20	Musk ketone	MP = 137°C	3.014
	Musk tibetine	MP = 136°C	3.831
	Myristicin	276	3.200
	Oxahexadecanolide-10	+300	4.336
	Oxahexadecanolide-11	MP = 35°C	4.336
25	Patchouli alcohol	285	4.530
	Phantolide	288	5.977
	Phenyl ethyl benzoate	300	4.058
	Phenyl ethyl phenyl acetate	325	3.767
	Phenyl heptanol	261	3.478
30	Phenyl hexanol	258	3.299
	alpha-Santalol	301	3.800

09856017-051601

	Thibetolide	280	6.246
	delta-Undecalactone	290	3.830
	gamma-Undecalactone	297	4.140
	Undecavertol (4-methyl-3-decen-5-ol)	250	3.690
5	Vetiveryl acetate	285	4.882
	Yara-yara	274	3.235
	Ylangene	250	6.268

10 (a) M.P. is melting point; these ingredients have a B.P. (boiling point) higher than about 250°C.

The preferred perfume compositions used in the present invention contain at least 4 different hydrophobic perfume ingredients, preferably at least 5 different hydrophobic perfume ingredients, more preferably at least 6 different hydrophobic perfume ingredients, and even more preferably at least 7 different hydrophobic perfume ingredients. Most common perfume ingredients which are derived from natural sources are composed of a multitude of components. When each such material is used in the formulation of the preferred perfume compositions of the present invention, it is counted as one single ingredient, for the purpose of defining the invention.

Low Odor Detection Threshold Perfume Ingredient

20 The composition can also contain low to moderate levels of low odor detection threshold materials, either dissolved in the aqueous phase to the extent of their water solubility or incorporated into the emulsion or dispersion with the other hydrophobic perfume ingredients. The odor detection threshold is the lowest vapor concentration of that material which can be olfactorily detected. The odor detection threshold and some odor detection threshold values are discussed in, e.g., "Standardized Human Olfactory Thresholds", M. Devos et al, IRL Press at Oxford University Press, 1990, and "Compilation of Odor and Taste Threshold Values Data", F. A. Fazzalari, editor, ASTM Data Series DS 48A, American Society for Testing and Materials, 1978, both of said publications being incorporated by reference. The use of small amounts of perfume ingredients that have low odor detection threshold values can improve perfume odor character. Perfume ingredients that have a significantly low detection threshold, useful in

the composition of the present invention, are selected from the group consisting of ambrox, bacdanol, benzyl salicylate, butyl anthranilate, cetalex, damascenone, alpha-damascone, gamma-dodecalactone, ebanol, herbavert, cis-3-hexenyl salicylate, alpha-ionone, beta-ionone, alpha-isomethylionone, linal, methyl nonyl ketone, gamma-undecalactone, undecylenic aldehyde, and mixtures thereof. These materials are preferably present at low levels, typically less than about 30%, preferably less than about 20%, more preferably less than about 15%, by weight of the total perfume compositions of the present invention. However, only low levels are required to provide an effect.

There are also hydrophilic ingredients that have a significantly low detection threshold, and are especially useful in the composition of the present invention. Examples of these ingredients are allyl amyl glycolate, anethole, benzyl acetone, calone, cinnamic alcohol, coumarin, cyclogalbanate, Cyclal C, cymal, 4-decenal, dihydro isojasmonate, ethyl anthranilate, ethyl-2-methyl butyrate, ethyl methylphenyl glycidate, ethyl vanillin, eugenol, flor acetate, florhydral, fructose, frutene, heliotropin, keone, indole, iso cyclo citral, isoeugenol, lylal, methyl heptene carbonate, linalool, methyl anthranilate, methyl dihydrojasmonate, methyl isobutenyl tetrahydropyran, methyl beta naphthyl ketone, beta naphthol methyl ether, nerol, para-anisic aldehyde, para hydroxy phenyl butanone, phenyl acetaldehyde, vanillin, and mixtures thereof. Use of low odor detection threshold perfume ingredients minimizes the level of organic material that is released into the atmosphere.

In order to provide compatibility with the cyclodextrin, the perfume ingredients which are hydrophobic, should be in a stable emulsion/dispersion. The particles of the emulsion/dispersion are preferably at least 0.01 micron in diameter, more preferably at least 0.05 micron in diameter. The emulsion is formed first and stabilized before the cyclodextrin is added. The preferred stabilizers are the siloxane surfactants described hereinafter; polymers containing both hydrophobic and hydrophilic portions; and cationic fabric softening actives in the form of stable vesicles in the desired particle size range. Thus, the composition comprises a stable hydrophobic perfume suspension (emulsion/dispersion) having a particle size of at least 0.01 micron, preferably at least 0.05 micron in diameter.

(a) The siloxane surfactant.

These surfactants are described in detail as (C) (b), below.

(b) The Block Copolymers

These stabilizers contain hydrophobic portions which preferably comprise monomers that are hydrophobic such as: poly butyl acrylate; poly acrylamide; poly butylaminoethyl methacrylate; poly octylacrylamide ; etc. and monomers that are hydrophilic, and preferably at least partially charged, such as: polyacrylate;. The molecular weight is preferably from about 1,000 to about 1,000,000, more preferably from about 5,000 to about 250,000, and even more preferably from about 10,000 to about 100,000. The ratio of hydrophilic portion to hydrophobic portion is preferably from 20/80 to about 90/10, more preferably from 30/70 to 75/25. The hydrophilic, preferably charged portion(s) of the polymer are preferably either in a terminal position or pendant on the hydrophobic portion, since the hydrophobic portion(s) are in the perfume and the hydrophilic portion(s) are in the water phase.

(c) The Softener Actives

Suitable cationic softener actives are described in detail in U.S. Pats.: 5,747,443, Wahl et al. issued May 5, 1998; 5,830,845, Trinh et al. issued Nov. 3, 1998; 5,759,990, Wahl et al. issued Jun. 2, 1998; 5,686,376, Rusche et al. issued Nov. 11, 1997; 5,500,138, Bacon et al., issued Mar. 19, 1996; 5,545,340, Wahl et al., issued Aug. 13, 1996; 5,804,219, Trinh et al. issued Sep. 8, 1998; and 4,661,269, Trinh et al., issued April 28, 1987, all of said patents being incorporated herein by reference. The softener actives are formed into a dispersion with the perfume before the cyclodextrin is added with the bulk of the water.

(C). CYCLODEXTRIN-COMPATIBLE SURFACTANT

The optional, but preferred, cyclodextrin-compatible surfactant B., provides a low surface tension that permits the composition to spread readily and more uniformly on hydrophobic surfaces like polyester and nylon. It has been found that the aqueous solution, without such a surfactant will not spread satisfactorily. The spreading of the composition also allows it to dry faster, so that the treated material is ready to use sooner. Furthermore, the composition containing a cyclodextrin-compatible surfactant can penetrate hydrophobic, oily soil better for improved malodor control. The composition containing a cyclodextrin-compatible surfactant also provides improved "in-wear"

electrostatic control. For concentrated compositions, the surfactant facilitates the dispersion of many actives such as antimicrobial actives and perfumes in the concentrated aqueous compositions.

The surfactant for use in providing the required low surface tension in the composition of the present invention should be cyclodextrin-compatible, that is it should not substantially form a complex with the cyclodextrin so as to diminish performance of the cyclodextrin and/or the surfactant. Complex formation diminishes both the ability of the cyclodextrin to absorb odors and the ability of the surfactant to lower the surface tension of the aqueous composition.

Suitable cyclodextrin-compatible surfactants can be readily identified by the absence of effect of cyclodextrin on the surface tension provided by the surfactant. This is achieved by determining the surface tension (in dyne/cm²) of aqueous solutions of the surfactant in the presence and in the absence of about 1% of a specific cyclodextrin in the solutions. The aqueous solutions contain surfactant at concentrations of approximately 0.5%, 0.1%, 0.01%, and 0.005%. The cyclodextrin can affect the surface activity of a surfactant by elevating the surface tension of the surfactant solution. If the surface tension at a given concentration in water differs by more than about 10% from the surface tension of the same surfactant in the 1% solution of the cyclodextrin, that is an indication of a strong interaction between the surfactant and the cyclodextrin. The preferred surfactants herein should have a surface tension in an aqueous solution that is different (lower) by less than about 10%, preferably less than about 5%, and more preferably less than about 1% from that of the same concentration solution containing 1% cyclodextrin.

(a) Block Copolymers

Nonlimiting examples of cyclodextrin-compatible nonionic surfactants include block copolymers of ethylene oxide and propylene oxide. Suitable block polyoxyethylene-polyoxypropylene polymeric surfactants, that are compatible with most cyclodextrins, include those based on ethylene glycol, propylene glycol, glycerol, trimethylolpropane and ethylenediamine as the initial reactive hydrogen compound. Polymeric compounds made from a sequential ethoxylation and propoxylation of initial compounds with a single reactive hydrogen atom, such as C₁₂₋₁₈ aliphatic alcohols, are not generally compatible with the cyclodextrin. Certain of the block polymer surfactant

compounds designated Pluronic[®] and Tetronic[®] by the BASF-Wyandotte Corp., Wyandotte, Michigan, are readily available.

Nonlimiting examples of cyclodextrin-compatible surfactants of this type include:

09856017-051601

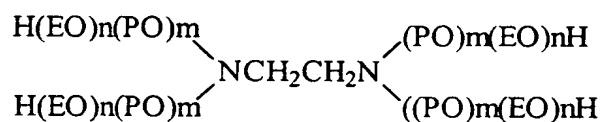
Pluronic Surfactants with the general formula $H(EO)_n(PO)_m(EO)_nH$,

wherein EO is an ethylene oxide group, PO is a propylene oxide group, and n and m are numbers that indicate the average number of the groups in the surfactants. Typical examples of cyclodextrin-compatible Pluronic surfactants are:

5	Name	Average MW	Average n	Average m
	L-101	3,800	4	59
	L-81	2,750	3	42
	L-44	2,200	10	23
	L-43	1,850	6	22
10	F-38	4,700	43	16
	P-84	4,200	19	43,

and mixtures thereof.

Tetronic Surfactants with the general formula:



wherein EO, PO, n, and m have the same meanings as above. Typical examples of cyclodextrin-compatible Tetronic surfactants are:

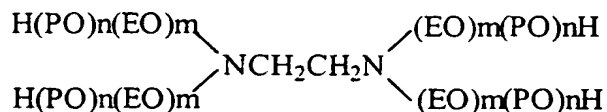
	Name	Average MW	Average n	Average m
20	901	4,700	3	18
	908	25,000	114	22,

and mixtures thereof.

"Reverse" Pluronic and Tetronic surfactants have the following general formulas:

Reverse Pluronic Surfactants $H(PO)_m(EO)_n(PO)_mH$

25 Reverse Tetronic Surfactants



wherein EO, PO, n, and m have the same meanings as above. Typical examples of cyclodextrin-compatible Reverse Pluronic and Reverse Tetronic surfactants are:

Reverse Pluronic surfactants:

09856017-051601

Name	Average MW	Average n	Average m
10 R5	1,950	8	22
25 R1	2,700	21	6

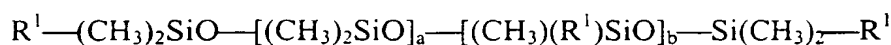
Reverse Tetronic surfactants

5 Name	Average MW	Average n	Average m
130 R2	7,740	9	26
70 R2	3,870	4	13

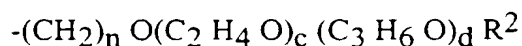
and mixtures thereof.

(b) Siloxane Surfactants

10 A preferred class of cyclodextrin-compatible nonionic surfactants are the polyalkyleneoxide polysiloxanes having a dimethyl polysiloxane hydrophobic moiety and one or more hydrophilic polyalkylene side chains and have the general formula:



15 wherein a + b are from about 1 to about 50, preferably from about 3 to about 30, more preferably from about 10 to about 25, and each R¹ is the same or different and is selected from the group consisting of methyl and a poly(ethyleneoxide/propyleneoxide) copolymer group having the general formula:



20 with at least one R¹ being a poly(ethyleneoxide/propyleneoxide) copolymer group, and wherein n is 3 or 4, preferably 3; total c (for all polyalkyleneoxy side groups) has a value of from 1 to about 100, preferably from about 6 to about 100; total d is from 0 to about 14, preferably from 0 to about 3; and more preferably d is 0; total c+d has a value of from about 5 to about 150, preferably from about 9 to about 100 and each R² is the same or different and is selected from the group consisting of hydrogen, an alkyl having 1 to 4
25 carbon atoms, and an acetyl group, preferably hydrogen and methyl group.

Examples of this type of surfactants are the Silwet[®] surfactants which are available OSi Specialties, Inc., Danbury, Connecticut. Representative Silwet surfactants are as follows.

Name	Average MW	Average a+b	Average total c
L-7608	600	1	9
L-7607	1,000	2	17
L-77	600	1	9
5 L-7605	6,000	20	99
L-7604	4,000	21	53
L-7600	4,000	11	68
L-7657	5,000	20	76
L-7602	3,000	20	29

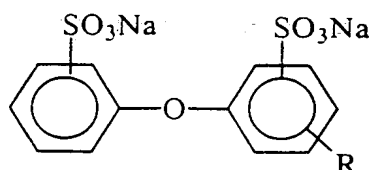
10 The molecular weight of the polyalkyleneoxy group (R^1) is less than or equal to about 10,000. Preferably, the molecular weight of the polyalkyleneoxy group is less than or equal to about 8,000, and most preferably ranges from about 300 to about 5,000. Thus, the values of c and d can be those numbers which provide molecular weights within these ranges. However, the number of ethyleneoxy units ($-C_2H_4O$) in the polyether chain (R^1) must be sufficient to render the polyalkyleneoxide polysiloxane water dispersible or water soluble. If propyleneoxy groups are present in the polyalkyleneoxy chain, they can be distributed randomly in the chain or exist as blocks. Preferred Silwet surfactants are L-7600, L-7602, L-7604, L-7605, L-7657, and mixtures thereof. Besides surface activity, polyalkyleneoxide polysiloxane surfactants can also provide other benefits, such as antistatic benefits, lubricity and softness to fabrics.

The preparation of polyalkyleneoxide polysiloxanes is well known in the art. Polyalkyleneoxide polysiloxanes of the present invention can be prepared according to the procedure set forth in U.S. Pat. No. 3,299,112, incorporated herein by reference. Typically, polyalkyleneoxide polysiloxanes of the surfactant blend of the present invention are readily prepared by an addition reaction between a hydrosiloxane (i.e., a siloxane containing silicon-bonded hydrogen) and an alkenyl ether (e.g., a vinyl, allyl, or methallyl ether) of an alkoxy or hydroxy end-blocked polyalkylene oxide). The reaction conditions employed in addition reactions of this type are well known in the art and in general involve heating the reactants (e.g., at a temperature of from about 85° C. to 110°

C.) in the presence of a platinum catalyst (e.g., chloroplatinic acid) and a solvent (e.g., toluene).

(c) Anionic Surfactants

Nonlimiting examples of cyclodextrin-compatible anionic surfactants are the
5 alkyl diphenyl oxide disulfonate, having the general formula:



wherein R is an alkyl group. Examples of this type of surfactants are available from the Dow Chemical Company under the trade name Dowfax[®] wherein R is a linear or branched C₆-C₁₆ alkyl group. An example of these cyclodextrin-compatible anionic
10 surfactant is Dowfax 3B2 with R being approximately a linear C₁₀ group. These anionic surfactants are preferably not used when the antimicrobial active or preservative, etc., is cationic to minimize the interaction with the cationic actives, since the effect of both surfactant and active are diminished.

The surfactants above are either weakly interactive with cyclodextrin (less than
15 5% elevation in surface tension, or non-interactive (less than 1% elevation in surface tension). Normal surfactants like sodium dodecyl sulfate and dodecanolpoly(6)ethoxylate are strongly interactive, with more than a 10% elevation in surface tension in the presence of a typical cyclodextrin like hydroxypropyl beta-cyclodextrin and methylated beta-cyclodextrin.

20 Typical levels of cyclodextrin-compatible surfactants in usage compositions are from about 0.01% to about 2%, preferably from about 0.03% to about 0.6%, more preferably from about 0.05% to about 0.3%, by weight of the composition. Typical levels of cyclodextrin-compatible surfactants in concentrated compositions are from about 0.1% to about 8%, preferably from about 0.2% to about 4%, more preferably from about 0.3%
25 to about 3%, by weight of the concentrated composition.

(D). CYCLODEXTRIN-COMPATIBLE ANTIMICROBIAL ACTIVE

The solubilized, water-soluble antimicrobial active, C., is useful in providing protection against organisms that become attached to the treated material. The antimicrobial should be cyclodextrin-compatible, e.g., not substantially forming complexes with the cyclodextrin in the odor absorbing composition. The free, uncomplexed antimicrobial, e.g., antibacterial, active provides an optimum antibacterial performance.

Sanitization of fabrics can be achieved by the compositions of the present invention containing, antimicrobial materials, e.g., antibacterial halogenated compounds, quaternary compounds, and phenolic compounds.

Biguanides. Some of the more robust cyclodextrin-compatible antimicrobial halogenated compounds which can function as disinfectants/sanitizers as well as finish product preservatives (vide infra), and are useful in the compositions of the present invention include 1,1'-hexamethylene bis(5-(p-chlorophenyl)biguanide), commonly known as chlorhexidine, and its salts, e.g., with hydrochloric, acetic and gluconic acids. The digluconate salt is highly water-soluble, about 70% in water, and the diacetate salt has a solubility of about 1.8% in water. When chlorhexidine is used as a sanitizer in the present invention it is typically present at a level of from about 0.001% to about 0.4%, preferably from about 0.002% to about 0.3%, and more preferably from about 0.05% to about 0.2%, by weight of the usage composition. In some cases, a level of from about 1% to about 2% may be needed for virucidal activity.

Other useful biguanide compounds include Cosmoci® CQ®, Vantocil® IB, including poly (hexamethylene biguanide) hydrochloride. Other useful cationic antimicrobial agents include the bis-biguanide alkanes. Usable water soluble salts of the above are chlorides, bromides, sulfates, alkyl sulfonates such as methyl sulfonate and ethyl sulfonate, phenylsulfonates such as p-methylphenyl sulfonates, nitrates, acetates, gluconates, and the like.

Examples of suitable bis biguanide compounds are chlorhexidine; 1,6-bis-(2-ethylhexylbiguanidohexane)dihydrochloride; 1,6-di-(N₁,N₁'-phenyldiguanido-N₅,N₅')-hexane tetrahydrochloride; 1,6-di-(N₁,N₁'-phenyl-N₁,N₁'-methyldiguanido-N₅,N₅')-

hexane dihydrochloride; 1,6-di(N_1, N_1' -o-chlorophenyldiguanido- N_5, N_5')-hexane dihydrochloride; 1,6-di(N_1, N_1' -2,6-dichlorophenyldiguanido- N_5, N_5')-hexane dihydrochloride; 1,6-di(N_1, N_1' -beta.-(p-methoxyphenyl) diguanido- N_5, N_5')-hexane dihydrochloride; 1,6-di(N_1, N_1' -.alpha.-methyl-.beta.-phenyldiguanido- N_5, N_5')-hexane dihydrochloride; 1,6-di(N_1, N_1' -p-nitrophenyldiguanido- N_5, N_5')-hexane dihydrochloride; omega.:omega'-.di-(N_1, N_1' -phenyldiguanido- N_5, N_5')-di-n-propylether dihydrochloride; omega:omega'-.di-(N_1, N_1' -p-chlorophenyldiguanido- N_5, N_5')-di-n-propylether tetrahydrochloride; 1,6-di(N_1, N_1' -2,4-dichlorophenyldiguanido- N_5, N_5')-hexane tetrahydrochloride; 1,6-di(N_1, N_1' -p-methylphenyldiguanido- N_5, N_5')-hexane dihydrochloride; 1,6-di(N_1, N_1' -2,4,5-trichlorophenyldiguanido- N_5, N_5')-hexane tetrahydrochloride; 1,6-di(N_1, N_1' -.alpha.-(p-chlorophenyl) ethyldiguanido- N_5, N_5') hexane dihydrochloride; omega.:omega'.di(N_1, N_1' -p-chlorophenyldiguanido- N_5, N_5')m-xylene dihydrochloride; 1,12-di(N_1, N_1' -p-chlorophenyldiguanido- N_5, N_5') dodecane dihydrochloride; 1,10-di(N_1, N_1' -phenyldiguanido- N_5, N_5')-decane tetrahydrochloride; 1,12-di(N_1, N_1' -phenyldiguanido- N_5, N_5') dodecane tetrahydrochloride; 1,6-di(N_1, N_1' -o-chlorophenyldiguanido- N_5, N_5')-hexane dihydrochloride; 1,6-di(N_1, N_1' -p-chlorophenyldiguanido- N_5, N_5')-hexane tetrahydrochloride; ethylene bis (1-tolyl biguanide); ethylene bis (p-tolyl biguanide); ethylene bis(3,5-dimethylphenyl biguanide); ethylene bis(p-tert-amylphenyl biguanide); ethylene bis(nonylphenyl biguanide); ethylene bis (phenyl biguanide); ethylene bis (N-butylphenyl biguanide); ethylene bis (2,5-diethoxyphenyl biguanide); ethylene bis(2,4-dimethylphenyl biguanide); ethylene bis(o-diphenylbiguanide); ethylene bis(mixed amyl naphthyl biguanide); N-butyl ethylene bis(phenylbiguanide); trimethylene bis(o-tolyl biguanide); N-butyl trimethylene bis(phenyl biguanide); and the corresponding pharmaceutically acceptable salts of all of the above such as the acetates; gluconates; hydrochlorides; hydrobromides; citrates; bisulfites; fluorides; polymaleates; N-coconutalkylsarcosinates; phosphites; hypophosphites; perfluorooctanoates; silicates; sorbates; salicylates; maleates; tartrates; fumarates; ethylenediaminetetraacetates; iminodiacetates; cinnamates; thiocyanates; arginates; pyromellitates;

09856017-051601

tetracarboxybutyrates; benzoates; glutarates; monofluorophosphates; and perfluoropropionates, and mixtures thereof. Preferred antimicrobials from this group are 1,6-di-(N₁,N₁'-phenyldiguanido-N₅,N₅')-hexane tetrahydrochloride; 1,6-di(N₁,N₁'-o-chlorophenyldiguanido-N₅,N₅')-hexane dihydrochloride; 1,6-di(N₁,N₁'-2,6-dichlorophenyldiguanido-N₅,N₅')hexane dihydrochloride; 1,6-di(N₁,N₁'-2,4-dichlorophenyldiguanido-N₅,N₅')hexane tetrahydrochloride; 1,6-di[N₁,N₁'-.alpha.-(p-chlorophenyl) ethyldiguanido-N₅,N₅'] hexane dihydrochloride; omega..omega.'di(N₁, N₁'-p-chlorophenyldiguanido-N₅,N₅')m-xylene dihydrochloride; 1,12-di(N₁,N₁'-p-chlorophenyldiguanido-N₅,N₅') dodecane dihydrochloride; 1,6-di(N₁,N₁'-o-chlorophenyldiguanido-N₅,N₅') hexane dihydrochloride; 1,6-di(N₁,N₁'-p-chlorophenyldiguanido-N₅,N₅')-hexane tetrahydrochloride; and mixtures thereof; more preferably, 1,6-di(N₁,N₁'-o-chlorophenyldiguanido-N₅,N₅')-hexane dihydrochloride; 1,6-di(N₁,N₁'-2,6-dichlorophenyldiguanido-N₅,N₅')hexane dihydrochloride; 1,6-di(N₁,N₁'-2,4-dichlorophenyldiguanido-N₅,N₅')hexane tetrahydrochloride; 1,6-di[N₁,N₁'-.alpha.-(p-chlorophenyl) ethyldiguanido-N₅,N₅'] hexane dihydrochloride; omega..omega.'di(N₁, N₁'-p-chlorophenyldiguanido-N₅,N₅')m-xylene dihydrochloride; 1,12-di(N₁,N₁'-p-chlorophenyldiguanido-N₅,N₅') dodecane dihydrochloride; 1,6-di(N₁,N₁'-o-chlorophenyldiguanido-N₅,N₅') hexane dihydrochloride; 1,6-di(N₁,N₁'-p-chlorophenyldiguanido-N₅,N₅')-hexane tetrahydrochloride; and mixtures thereof. As stated hereinbefore, the bis biguanide of choice is chlorhexidine its salts, e.g., digluconate, dihydrochloride, diacetate, and mixtures thereof.

Quaternary Compounds. A wide range of quaternary compounds can also be used as antimicrobial actives, in conjunction with the preferred surfactants, for compositions of the present invention that do not contain cyclodextrin. Non-limiting examples of useful quaternary compounds include: (1) benzalkonium chlorides and/or substituted benzalkonium chlorides such as commercially available Barquat[®] (available from Lonza), Maquat[®] (available from Mason), Variquat[®] (available from Witco/Sherex), and Hyamine[®] (available from Lonza); (2) di(C₆-C₁₄)alkyl di short chain (C₁₋₄ alkyl and/or

hydroxyalkyl) quaternary such as Bardac[®] products of Lonza, (3) N-(3-chloroallyl) hexaminium chlorides such as Dowicide[®] and Dowicil[®] available from Dow; (4) benzethonium chloride such as Hyamine[®] 1622 from Rohm & Haas; (5) methylbenzethonium chloride represented by Hyamine[®] 10X supplied by Rohm & Haas, (6) cetylpyridinium chloride such as Cepacol chloride available from Merrell Labs. Examples of the preferred dialkyl quaternary compounds are di(C₈-C₁₂)dialkyl dimethyl ammonium chloride, such as didecyldimethylammonium chloride (Bardac 22), and dioctyldimethylammonium chloride (Bardac 2050). Typical concentrations for biocidal effectiveness of these quaternary compounds range from about 0.001% to about 0.8%, preferably from about 0.005% to about 0.3%, more preferably from about 0.01% to about 0.2%, and even more preferably from about 0.03% to about 0.1%, by weight of the usage composition. The corresponding concentrations for the concentrated compositions are from about 0.003% to about 2%, preferably from about 0.006% to about 1.2%, and more preferably from about 0.1% to about 0.8% by weight of the concentrated compositions.

The surfactants, when added to the antimicrobials tend to provide improved antimicrobial action. This is especially true for the siloxane surfactants, and especially when the siloxane surfactants are combined with the chlorhexidine antimicrobial actives.

(E). LOW MOLECULAR WEIGHT POLYOLS

Low molecular weight polyols with relatively high boiling points, as compared to water, such as ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, dipropylene glycol, and/or glycerine are preferred optional ingredients for improving odor control performance of the composition of the present invention. Not to be bound by theory, it is believed that the incorporation of a small amount of low molecular weight glycols into the composition of the present invention enhances the formation of the cyclodextrin inclusion complexes as the fabric dries.

It is believed that the polyols' ability to remain on the fabric for a longer period of time than water, as the fabric dries allows it to form ternary complexes with the cyclodextrin and some malodorous molecules. The addition of the glycols is believed to fill up void space in the cyclodextrin cavity that is unable to be totally filled by some

malodor molecules of relatively smaller sizes. Preferably the glycol used is glycerine, ethylene glycol, propylene glycol, dipropylene glycol or mixtures thereof, more preferably ethylene glycol and propylene glycol. Cyclodextrins prepared by processes that result in a level of such polyols are highly desirable, since they can be used without removal of the polyols.

Some polyols, e.g., dipropylene glycol, are also useful to facilitate the solubilization of some perfume ingredients in the composition of the present invention.

Typically, glycol is added to the composition of the present invention at a level of from about 0.01% to about 3%, by weight of the composition, preferably from about 0.05% to about 1%, more preferably from about 0.1% to about 0.5%, by weight of the composition. The preferred weight ratio of low molecular weight polyol to cyclodextrin is from about 2:1,000 to about 20:100, more preferably from about 3:1,000 to about 15:100, even more preferably from about 5:1,000 to about 10:100, and most preferably from about 1:100 to about 7:100.

(F). OPTIONAL AMINOCARBOXYLATE CHELATORS

Chelators, e.g., ethylenediaminetetraacetic acid (EDTA), hydroxyethylenediaminetriacetic acid, diethylenetriaminepentaacetic acid, and other aminocarboxylate chelators, and mixtures thereof, and their salts, and mixtures thereof, can optionally be used to increase antimicrobial and preservative effectiveness against Gram-negative bacteria, especially Pseudomonas species. Although sensitivity to EDTA and other aminocarboxylate chelators is mainly a characteristic of Pseudomonas species, other bacterial species highly susceptible to chelators include Achromobacter, Alcaligenes, Azotobacter, Escherichia, Salmonella, Spirillum, and Vibrio. Other groups of organisms also show increased sensitivities to these chelators, including fungi and yeasts. Furthermore, aminocarboxylate chelators can help, e.g., maintaining product clarity, protecting fragrance and perfume components, and preventing rancidity and off odors.

Although these aminocarboxylate chelators may not be potent biocides in their own right, they function as potentiators for improving the performance of other antimicrobials/preservatives in the compositions of the present invention. Aminocarboxylate chelators can potentiate the performance of many of the cationic, anionic, and nonionic antimicrobials/preservatives, phenolic compounds, and

isothiazolinones, that are used as antimicrobials/preservatives in the composition of the present invention. Nonlimiting examples of cationic antimicrobials/preservatives potentiated by aminocarboxylate chelators in solutions are chlorhexidine salts (including digluconate, diacetate, and dihydrochloride salts), and Quaternium-15, also known as Dowicil 200, Dowicide Q, Preventol D1, benalkonium chloride, cetrimonium, myristalkonium chloride, cetylpyridinium chloride, lauryl pyridinium chloride, and the like. Nonlimiting examples of useful anionic antimicrobials/preservatives which are enhanced by aminocarboxylate chelators are sorbic acid and potassium sorbate. Nonlimiting examples of useful nonionic antimicrobials/preservatives which are potentiated by aminocarboxylate chelators are DMDM hydantoin, phenethyl alcohol, monolaurin, imidazolidinyl urea, and Bronopol (2-bromo-2-nitropropane-1,3-diol).

Examples of useful phenolic antimicrobials/preservatives potentiated by these chelators are chloroxylonol, phenol, tert-butyl hydroxyanisole, salicylic acid, resorcinol, and sodium o-phenyl phenate. Nonlimiting examples of isothiazolinone antimicrobials/preservatives which are enhanced by aminocarboxylate chelators are Kathon, Proxel and Promexal.

The optional chelators are present in the compositions of this invention at levels of, typically, from about 0.01% to about 0.3%, more preferably from about 0.02% to about 0.1%, most preferably from about 0.02% to about 0.05% by weight of the usage compositions to provide antimicrobial efficacy in this invention.

Free, uncomplexed aminocarboxylate chelators are required to potentiate the efficacy of the antimicrobials. Thus, when excess alkaline earth (especially calcium and magnesium) and transitional metals (iron, manganese, copper, and others) are present, free chelators are not available and antimicrobial potentiation is not observed. In the case where significant water hardness or transitional metals are available or where product esthetics require a specified chelator level, higher levels may be required to allow for the availability of free, uncomplexed aminocarboxylate chelators to function as antimicrobial/preservative potentiators.

(G) METAL SALTS

Optionally, but highly preferred, the present invention can include metallic salts for added odor absorption and/or antimicrobial benefit for the cyclodextrin solution. The

metallic salts are selected from the group consisting of copper salts, zinc salts, and mixtures thereof.

Copper salts have some antimicrobial benefits. Specifically, cupric abietate acts as a fungicide, copper acetate acts as a mildew inhibitor, cupric chloride acts as a fungicide, copper lactate acts as a fungicide, and copper sulfate acts as a germicide. Copper salts also possess some malodor control abilities. See U. S. Pat. No. 3,172,817, Leupold, et al., which discloses deodorizing compositions for treating disposable articles, comprising at least slightly water-soluble salts of acylacetone, including copper salts and zinc salts, all of said patents are incorporated herein by reference.

The preferred zinc salts possess malodor control abilities. Zinc has been used most often for its ability to ameliorate malodor, e.g., in mouth wash products, as disclosed in U.S. Pat. Nos. 4,325,939, issued Apr. 20, 1982 and 4,469,674, issued Sept. 4, 1983, to N. B. Shah, et al., all of which are incorporated herein by reference. Highly-ionized and soluble zinc salts such as zinc chloride, provide the best source of zinc ions. Zinc borate functions as a fungistat and a mildew inhibitor, zinc caprylate functions as a fungicide, zinc chloride provides antiseptic and deodorant benefits, zinc ricinoleate functions as a fungicide, zinc sulfate heptahydrate functions as a fungicide and zinc undecylenate functions as a fungistat.

Preferably the metallic salts are water-soluble zinc salts, copper salts or mixtures thereof, and more preferably zinc salts, especially ZnCl_2 . These salts are preferably present in the present invention primarily to absorb amine and sulfur-containing compounds that have molecular sizes too small to be effectively complexed with the cyclodextrin molecules. Low molecular weight sulfur-containing materials, e.g., sulfide and mercaptans, are components of many types of malodors, e.g., food odors (garlic, onion), body/perspiration odor, breath odor, etc. Low molecular weight amines are also components of many malodors, e.g., food odors, body odors, urine, etc.

When metallic salts are added to the composition of the present invention they are typically present at a level of from about 0.1% to about 10%, preferably from about 0.2% to about 8%, more preferably from about 0.3% to about 5% by weight of the usage composition. When zinc salts are used as the metallic salt, and a clear solution is desired,

it is preferable that the pH of the solution is adjusted to less than about 7, more preferably less than about 6, most preferably, less than about 5, in order to keep the solution clear.

(H). HUMECTANT

Optionally, the composition can contain a small amount of humectant, such as glycerine, or inorganic hygroscopic material, to provide slower drying for clothing/fabrics treated with the compositions, to allow time for any wrinkles to disappear when the clothing/fabrics are hung to dry. For most purposes, this is preferably not present, since normally the user wants the clothing/fabrics to dry sooner.

When a humectant is used, it is present in the composition in an amount of from about 0.01% to about 10%, preferably from about 0.05% to about 5%, more preferably from about 0.1% to about 2%, by weight of the usage composition.

(I) CARRIER

Aqueous solutions that contain up to 5% alcohol are preferred for odor control. The dilute aqueous solution provides the maximum separation of cyclodextrin molecules on the fabric and thereby maximizes the chance that an odor molecule will interact with a cyclodextrin molecule.

The preferred carrier of the present invention is water. The water which is used can be distilled, deionized, or tap water. Water not only serves as the liquid carrier for the cyclodextrins, but it also facilitates the complexation reaction between the cyclodextrin molecules and any malodorous molecules that are on the fabric when it is treated. It has recently been discovered that water has an unexpected odor controlling effect of its own. It has been discovered that the intensity of the odor generated by some polar, low molecular weight organic amines, acids, and mercaptans is reduced when the odor-contaminated fabrics are treated with an aqueous solution. Not to be bound by theory, it is believed that water solubilizes and depresses the vapor pressure of these polar, low molecular weight organic molecules, thus reducing their odor intensity.

(J) OTHER OPTIONAL INGREDIENTS

The composition of the present invention can optionally contain adjunct odor-controlling materials, enzymes, chelating agents, antistatic agents, insect and moth repelling agents, colorants, especially bluing agents, antioxidants, and mixtures thereof in addition to the cyclodextrin molecules. The total level of optional ingredients is low,

preferably less than about 5%, more preferably less than about 3%, and even more preferably less than about 2%, by weight of the usage composition. These optional ingredients exclude the other ingredients specifically mentioned hereinbefore. Incorporating adjunct odor-controlling materials can enhance the capacity of the cyclodextrin to control odors as well as broaden the range of odor types and molecule sizes which can be controlled. Such materials include, for example, metallic salts, water-soluble cationic and anionic polymers, zeolites, water-soluble bicarbonate salts, and mixtures thereof.

(1) Water Soluble Polymers

Some water-soluble polymers, e.g., water-soluble cationic polymer and water-soluble anionic polymers can be used in the composition of the present invention to provide additional odor control benefits.

a. Cationic polymers, e.g., polvamines

Water-soluble cationic polymers, e.g., those containing amino functionalities, amido functionalities, and mixtures thereof, are useful in the present invention to control certain acid-type odors.

b. Anionic polymers, e.g., polyacrylic acid

Water-soluble anionic polymers, e.g., polyacrylic acids and their water-soluble salts are useful in the present invention to control certain amine-type odors. Preferred polyacrylic acids and their alkali metal salts have an average molecular weight of less than about 20,000, more preferably less than 5,000. Polymers containing sulfonic acid groups, phosphoric acid groups, phosphonic acid groups, and their water-soluble salts, and mixtures thereof, and mixtures with carboxylic acid and carboxylate groups, are also suitable.

Water-soluble polymers containing both cationic and anionic functionalities are also suitable. Examples of these polymers are given in U.S. Pat. 4,909,986, issued March 20, 1990 to N. Kobayashi and A. Kawazoe, incorporated herein by reference. Another example of water-soluble polymers containing both cationic and anionic functionalities is a copolymer of dimethyldiallyl ammonium chloride and acrylic acid, commercially available under the trade name Merquat 280® from Calgon.

When a water-soluble polymer is used it is typically present at a level of from about 0.001% to about 3%, preferably from about 0.005% to about 2%, more preferably from about 0.01% to about 1%, and even more preferably from about 0.05% to about 0.5%, by weight of the usage composition.

5 **(2). Soluble Carbonate and/or Bicarbonate Salts**

Water-soluble alkali metal carbonate and/or bicarbonate salts, such as sodium bicarbonate, potassium bicarbonate, potassium carbonate, cesium carbonate, sodium carbonate, and mixtures thereof can be added to the composition of the present invention in order to help to control certain acid-type odors. Preferred salts are sodium carbonate monohydrate, potassium carbonate, sodium bicarbonate, potassium bicarbonate, and mixtures thereof. When these salts are added to the composition of the present invention, they are typically present at a level of from about 0.1% to about 5%, preferably from about 0.2% to about 3%, more preferably from about 0.3% to about 2%, by weight of the composition. When these salts are added to the composition of the present invention it is preferably that incompatible metal salts not be present in the invention. Preferably, when these salts are used the composition should be essentially free of zinc and other incompatible metal ions, e.g., Ca, Fe, Ba, etc. which form water-insoluble salts.

15 **(3). Enzymes**

Enzymes can be used to control certain types of malodor, especially malodor from urine and other types of excretions, including regurgitated materials. Proteases are especially desirable. The activity of commercial enzymes depends very much on the type and purity of the enzyme being considered. Enzymes that are water soluble proteases like pepsin, tripsin, ficin, bromelin, papain, rennin, and mixtures thereof are particularly useful.

25 Enzymes are normally incorporated at levels sufficient to provide up to about 5 mg by weight, preferably from about 0.001 mg to about 3 mg, more preferably from about 0.002 mg to about 1 mg, of active enzyme per gram of the aqueous compositions. Stated otherwise, the aqueous compositions herein can comprise from about 0.0001% to about 0.5%, preferably from about 0.001% to about 0.3%, more preferably from about 0.005% to about 0.2% by weight of a commercial enzyme preparation. Protease enzymes are

30

09856017-051601

usually present in such commercial preparations at levels sufficient to provide from 0.0005 to 0.1 Anson units (AU) of activity per gram of aqueous composition.

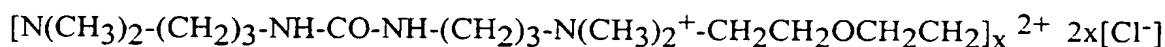
Nonlimiting examples of suitable, commercially available, water soluble proteases are pepsin, tripsin, ficin, bromelin, papain, rennin, and mixtures thereof. Papain can be isolated, e.g., from papaya latex, and is available commercially in the purified form of up to, e.g., about 80% protein, or cruder, technical grade of much lower activity. Other suitable examples of proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis*. Another suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold by Novo Industries A/S under the registered trade name ESPERASE®. The preparation of this enzyme and analogous enzymes is described in British Patent Specification No. 1,243,784 of Novo. Proteolytic enzymes suitable for removing protein-based stains that are commercially available include those sold under the trade names ALCALASE® and SAVINASE® by Novo Industries A/S (Denmark) and MAXATASE® by International Bio-Synthetics, Inc. (The Netherlands). Other proteases include Protease A (see European Patent Application 130,756, published January 9, 1985); Protease B (see European Patent Application Serial No. 87303761.8, filed April 28, 1987, and European Patent Application 130,756, Bott et al, published January 9, 1985); and proteases made by Genencor International, Inc., according to one or more of the following patents: Caldwell et al, U.S. Patent Nos. 5,185,258, 5,204,015 and 5,244,791.

A wide range of enzyme materials and means for their incorporation into liquid compositions are also disclosed in U.S. Patent 3,553,139, issued January 5, 1971 to McCarty et al. Enzymes are further disclosed in U.S. Patent 4,101,457, Place et al, issued July 18, 1978, and in U.S. Patent 4,507,219, Hughes, issued March 26, 1985. Other enzyme materials useful for liquid formulations, and their incorporation into such formulations, are disclosed in U.S. Patent 4,261,868, Hora et al, issued April 14, 1981. Enzymes can be stabilized by various techniques, e.g., those disclosed and exemplified in U.S. Patent 3,600,319, issued August 17, 1971 to Gedge, et al., European Patent Application Publication No. 0 199 405, Application No. 86200586.5, published October 29, 1986, Venegas, and in U.S. Patent 3,519,570. All of the above patents and applications are incorporated herein, at least in pertinent part.

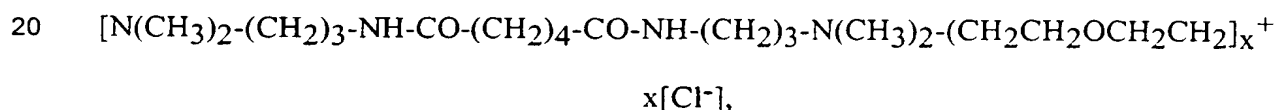
Enzyme-polyethylene glycol conjugates are also preferred. Such polyethylene glycol (PEG) derivatives of enzymes, wherein the PEG or alkoxy-PEG moieties are coupled to the protein molecule through, e.g., secondary amine linkages. Suitable derivatization decreases immunogenicity, thus minimizes allergic reactions, while still maintains some enzymatic activity. An example of protease-PEG's is PEG-subtilisin Carlsberg from *B. lichenniformis* coupled to methoxy-PEGs through secondary amine linkage, and is available from Sigma-Aldrich Corp., St Louis, Missouri.

(4). Antistatic Agents

The composition of the present invention can optionally contain an effective amount of antistatic agent to provide the treated clothes with in-wear static control. Preferred antistatic agents are those that are water soluble in at least an effective amount, such that the composition remains a clear solution, and are compatible with cyclodextrin. Nonlimiting examples of these antistatic agents are polymeric quaternary ammonium salts, such as polymers conforming to the general formula:



available under the trade name Mirapol A-15[®] from Rhône-Poulenc, and



available under the trade name Mirapol AD-1[®] from Rhône-Poulenc, quaternized polyethyleneimines, vinylpyrrolidone/methacrylamidopropyltrimethylammonium chloride copolymer, available under the trade name Gafquat HS-100[®] from GAF; triethonium hydrolyzed collagen ethosulfate, available under the trade name Quat-Pro E[®] from Maybrook; neutralized sulfonated polystyrene, available, e.g., under the trade name Versa TL-130[®] from Alco Chemical, neutralized sulfonated styrene/maleic anhydride

copolymers, available, e.g., under the trade name Versa TL-4[®] from Alco Chemical; polyethylene glycols; and mixtures thereof.

It is preferred that a no foaming, or low foaming, agent is used, to avoid foam formation during fabric treatment. It is also preferred that polyethoxylated agents such as polyethylene glycol or Variquat 66[®] are not used when alpha-cyclodextrin is used. The polyethoxylate groups have a strong affinity to, and readily complex with, alpha-cyclodextrin which in turn depletes the uncomplexed cyclodextrin available for odor control.

When an antistatic agent is used it is typically present at a level of from about 0.05% to about 10%, preferably from about 0.1% to about 5%, more preferably from about 0.3% to about 3%, by weight of the usage composition.

(5). Insect and/or Moth Repelling Agent

The composition of the present invention can optionally contain an effective amount of insect and/or moth repelling agents. Typical insect and moth repelling agents are pheromones, such as anti-aggregation pheromones, and other natural and/or synthetic ingredients. Preferred insect and moth repellent agents useful in the composition of the present invention are perfume ingredients, such as citronellol, citronellal, citral, linalool, cedar extract, geranium oil, sandalwood oil, 2-(diethylphenoxy)ethanol, 1-dodecene, etc. Other examples of insect and/or moth repellents useful in the composition of the present invention are disclosed in U.S. Pat. Nos. 4,449,987, 4,693,890, 4,696,676, 4,933,371, 5,030,660, 5,196,200, and in "Semio Activity of Flavor and Fragrance Molecules on Various Insect Species", B.D. Mookherjee et al., published in Bioactive Volatile Compounds from Plants, ASC Symposium Series 525, R. Teranishi, R.G. Buttery, and H. Sugisawa, 1993, pp. 35-48, all of said patents and publications being incorporated herein by reference. When an insect and/or moth repellent is used it is typically present at a level of from about 0.005% to about 3%, by weight of the usage composition.

(6). Additional Odor Absorbers

When the clarity of the solution is not needed, and the solution is not sprayed on fabrics, other optional odor absorbing materials, e.g., zeolites and/or activated carbon, can also be used.

(a). Zeolites

A preferred class of zeolites is characterized as "intermediate" silicate/aluminate zeolites. The intermediate zeolites are characterized by $\text{SiO}_2/\text{AlO}_2$ molar ratios of less than about 10. Preferably the molar ratio of $\text{SiO}_2/\text{AlO}_2$ ranges from about 2 to about 10. The intermediate zeolites have an advantage over the "high" zeolites. The intermediate zeolites have a higher affinity for amine-type odors, they are more weight efficient for odor absorption because they have a larger surface area, and they are more moisture tolerant and retain more of their odor absorbing capacity in water than the high zeolites. A wide variety of intermediate zeolites suitable for use herein are commercially available as Valfor[®] CP301-68, Valfor[®] 300-63, Valfor[®] CP300-35, and Valfor[®] CP300-56, available from PQ Corporation, and the CBV100[®] series of zeolites from Conteka.

Zeolite materials marketed under the trade name Abscents[®] and Smellrite[®], available from The Union Carbide Corporation and UOP are also preferred. These materials are typically available as a white powder in the 3-5 micron particle size range. Such materials are preferred over the intermediate zeolites for control of sulfur-containing odors, e.g., thiols, mercaptans.

(b). Activated Carbon

The carbon material suitable for use in the present invention is the material well known in commercial practice as an absorbent for organic molecules and/or for air purification purposes. Often, such carbon material is referred to as "activated" carbon or "activated" charcoal. Such carbon is available from commercial sources under such trade names as; Calgon-Type CPG[®]; Type PCB[®]; Type SGL[®]; Type CAL[®]; and Type OL[®].

(7). Colorant

Colorants and dyes, especially bluing agents, can be optionally added to the odor absorbing compositions for visual appeal and performance impression. When colorants are used, they are used at extremely low levels to avoid fabric staining. Preferred colorants for use in the present compositions are highly water-soluble dyes, e.g., Liquitint[®] dyes available from Milliken Chemical Co. Non-limiting examples of suitable dyes are, Liquitint Blue HP[®], Liquitint Blue 65[®], Liquitint Patent Blue[®], Liquitint Royal

Blue[®], Liquitint Experimental Yellow 8949-43[®], Liquitint Green HMC[®], Liquitint Yellow II[®], and mixtures thereof, preferably Liquitint Blue HP[®], Liquitint Blue 65[®], Liquitint Patent Blue[®], Liquitint Royal Blue[®], Liquitint Experimental Yellow 8949-43[®], and mixtures thereof.

5 (8). **Optional Preservative**

Optionally, but preferably, solubilized, water-soluble, antimicrobial preservative can be added to the composition of the present invention if the antimicrobial material C. is not sufficient, or is not present, because cyclodextrin molecules are made up of varying numbers of glucose units which can make them a prime breeding ground for certain microorganisms, especially when in aqueous compositions. This drawback can lead to the problem of storage stability of cyclodextrin solutions for any significant length of time. Contamination by certain microorganisms with subsequent microbial growth can result in an unsightly and/or malodorous solution. Because microbial growth in cyclodextrin solutions is highly objectionable when it occurs, it is highly preferable to include a solubilized, water-soluble, antimicrobial preservative, which is effective for inhibiting and/or regulating microbial growth in order to increase storage stability of the preferably clear, aqueous odor-absorbing solution containing water-soluble cyclodextrin.

Typical microorganisms that can be found in cyclodextrin supplies and whose growth can be found in the presence of cyclodextrin in aqueous cyclodextrin solutions include bacteria, e.g., Bacillus thuringiensis (cereus group) and Bacillus sphaericus; and fungi, e.g., Aspergillus ustus. Bacillus sphaericus is one of the most numerous members of Bacillus species in soils. Aspergillus ustus is common in grains and flours which are raw materials to produce cyclodextrins. Microorganisms such as Escherichia coli and Pseudomonas aeruginosa are found in some water sources, and can be introduced during the preparation of cyclodextrin solutions. Other Pseudomonas species, such as P. cepacia, are typical microbial contaminants in surfactant manufacturing facilities and may readily contaminate packed finished products. Typical other bacterial contaminants may include Burkholderia, Enterobacter and Gluconobacter species. Representative fungal species which may be associated with agricultural soils, crops and in the case of this invention, corn products such as cyclodextrins include Aspergillus, Absidia, Penicillium, Paecilomyces, and other species.

It is preferable to use a broad spectrum preservative, e.g., one that is effective on both bacteria (both gram positive and gram negative) and fungi. A limited spectrum preservative, e.g., one that is only effective on a single group of microorganisms, e.g., fungi, can be used in combination with a broad spectrum preservative or other limited spectrum preservatives with complimentary and/or supplementary activity. A mixture of broad spectrum preservatives can also be used. In some cases where a specific group of microbial contaminants is problematic (such as Gram negatives), aminocarboxylate chelators may be used alone or as potentiators in conjunction with other preservatives. These chelators which include, e.g., ethylenediaminetetraacetic acid (EDTA), hydroxyethylenediaminetriacetic acid, diethylenetriaminepentaacetic acid, and other aminocarboxylate chelators, and mixtures thereof, and their salts, and mixtures thereof, can increase preservative effectiveness against Gram-negative bacteria, especially *Pseudomonas* species.

Antimicrobial preservatives useful in the present invention include biocidal compounds, i.e., substances that kill microorganisms, or biostatic compounds, i.e., substances that inhibit and/or regulate the growth of microorganisms.

Preferred antimicrobial preservatives are those that are water-soluble and are effective at low levels because the organic preservatives can form inclusion complexes with the cyclodextrin molecules and compete with the malodorous molecules for the cyclodextrin cavities, thus rendering the cyclodextrins ineffective as odor controlling actives. Water-soluble preservatives useful in the present invention are those that have a solubility in water of at least about 0.3 g per 100 ml of water, i.e., greater than about 0.3% at room temperature, preferably greater than about 0.5% at room temperature. These types of preservatives have a lower affinity to the cyclodextrin cavity, at least in the aqueous phase, and are therefore more available to provide antimicrobial activity. Preservatives with a water-solubility of less than about 0.3% and a molecular structure that readily fits into the cyclodextrin cavity, have a greater tendency to form inclusion complexes with the cyclodextrin molecules, thus rendering the preservative less effective to control microbes in the cyclodextrin solution. Therefore, many well known preservatives such as short chain alkyl esters of p-hydroxybenzoic acid, commonly known as parabens; N-(4-chlorophenyl)-N'-(3,4-dichlorophenyl) urea, also known as 3,4,4'-

trichlorocarbanilide or triclocarban; 2,4,4'-trichloro-2'-hydroxy diphenyl ether, commonly known as triclosan are not preferred in the present invention since they are relatively ineffective when used in conjunction with cyclodextrin.

The water-soluble antimicrobial preservative in the present invention is included at an effective amount. The term "effective amount" as herein defined means a level sufficient to prevent spoilage, or prevent growth of inadvertently added microorganisms, for a specific period of time. In other words, the preservative is not being used to kill microorganisms on the surface onto which the composition is deposited in order to eliminate odors produced by microorganisms. Instead, it is preferably being used to prevent spoilage of the cyclodextrin solution in order to increase the shelf-life of the composition. Preferred levels of preservative are from about 0.0001% to about 0.5%, more preferably from about 0.0002% to about 0.2%, most preferably from about 0.0003% to about 0.1%, by weight of the usage composition.

In order to reserve most of the cyclodextrins for odor control, the cyclodextrin to preservative molar ratio should be greater than about 5:1, preferably greater than about 10:1, more preferably greater than about 50:1, even more preferably greater than about 100:1.

The preservative can be any organic preservative material which will not cause damage to fabric appearance, e.g., discoloration, coloration, bleaching. Preferred water-soluble preservatives include organic sulfur compounds, halogenated compounds, cyclic organic nitrogen compounds, low molecular weight aldehydes, quaternary ammonium compounds, dehydroacetic acid, phenyl and phenolic compounds, and mixtures thereof.

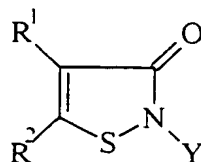
The following are non-limiting examples of preferred water-soluble preservatives for use in the present invention.

(A). Organic Sulfur Compounds

Preferred water-soluble preservatives for use in the present invention are organic sulfur compounds. Some non-limiting examples of organic sulfur compounds suitable for use in the present invention are:

(a) 3-Isothiazolone Compounds

A preferred preservative is an antimicrobial, organic preservative containing 3-isothiazolone groups having the formula:



wherein

Y is an unsubstituted alkyl, alkenyl, or alkynyl group of from about 1 to about 18 carbon atoms, an unsubstituted or substituted cycloalkyl group having from about a 3 to about a 6 carbon ring and up to 12 carbon atoms, an unsubstituted or substituted aralkyl group of up to about 10 carbon atoms, or an unsubstituted or substituted aryl group of up to about 10 carbon atoms;

R¹ is hydrogen, halogen, or a (C₁-C₄) alkyl group; and

R² is hydrogen, halogen, or a (C₁-C₄) alkyl group.

Preferably, when Y is methyl or ethyl, R¹ and R² should not both be hydrogen. Salts of these compounds formed by reacting the compound with acids such as hydrochloric, nitric, sulfuric, etc. are also suitable.

This class of compounds is disclosed in U.S. Pat. No. 4,265,899, Lewis et al., issued May 5, 1981, and incorporated herein by reference. Examples of said compounds are: 5-chloro-2-methyl-4-isothiazolin-3-one; 2-n-butyl-3-isothiazolone; 2-benzyl-3-isothiazolone; 2-phenyl-3-isothiazolone, 2-methyl-4,5-dichloroisothiazolone; ; 5-chloro-2-methyl-3-isothiazolone; 2-methyl-4-isothiazolin-3-one; and mixtures thereof. A preferred preservative is a water-soluble mixture of 5-chloro-2-methyl-4-isothiazolin-3-one and 2-methyl-4-isothiazolin-3-one, more preferably a mixture of about 77% 5-chloro-2-methyl-4-isothiazolin-3-one and about 23% 2-methyl-4-isothiazolin-3-one, a broad spectrum preservative available as a 1.5% aqueous solution under the trade name Kathon[®] CG by Rohm and Haas Company.

When Kathon[®] is used as the preservative in the present invention it is present at a level of from about 0.0001% to about 0.01%, preferably from about 0.0002% to about 0.005%, more preferably from about 0.0003% to about 0.003%, most preferably from about 0.0004% to about 0.002%, by weight of the composition.

Other isothiazolins include 1,2-benzisothiazolin-3-one, available under the trade name Proxel[®] products; and 2-methyl-4,5-trimethylene-4-isothiazolin-3-one, available under the trade name Promexal[®]. Both Proxel and Promexal are available from Zeneca. They have stability over a wide pH range (i.e., 4-12). Neither contain active halogen and are not formaldehyde releasing preservatives. Both Proxel and Promexal are effective against typical Gram negative and positive bacteria, fungi and yeasts when used at a level from about 0.001% to about 0.5%, preferably from about 0.005% to about 0.05%, and most preferably from about 0.01% to about 0.02% by weight of the usage composition.

(b) Sodium Pyrithione

Another preferred organic sulfur preservative is sodium pyrithione, with water solubility of about 50%. When sodium pyrithione is used as the preservative in the present invention it is typically present at a level of from about 0.0001% to about 0.01%, preferably from about 0.0002% to about 0.005%, more preferably from about 0.0003% to about 0.003%, by weight of the usage composition.

Mixtures of the preferred organic sulfur compounds can also be used as the preservative in the present invention.

(B). Halogenated Compounds

Preferred preservatives for use in the present invention are halogenated compounds. Some non-limiting examples of halogenated compounds suitable for use in the present invention are:

5-bromo-5-nitro-1,3-dioxane, available under the trade name Bronidox L[®] from Henkel. Bronidox L[®] has a solubility of about 0.46% in water. When Bronidox is used as the preservative in the present invention it is typically present at a level of from about 0.0005% to about 0.02%, preferably from about 0.001% to about 0.01%, by weight of the usage composition;

2-bromo-2-nitropropane-1,3-diol, available under the trade name Bronopol[®] from Inolex can be used as the preservative in the present invention. Bronopol has a solubility of about 25% in water. When Bronopol is used as the preservative in the present invention it is typically present at a level of from about 0.002% to about 0.1%, preferably from about 0.005% to about 0.05%, by weight of the usage composition;

1,1'-hexamethylene bis(5-(p-chlorophenyl)biguanide), commonly known as chlorhexidine, and its salts, e.g., with acetic and gluconic acids can be used as a preservative in the present invention. The digluconate salt is highly water-soluble, about 70% in water, and the diacetate salt has a solubility of about 1.8% in water. When
5 chlorhexidine is used as the preservative in the present invention it is typically present at a level of from about 0.0001% to about 0.04%, preferably from about 0.0005% to about 0.01%, by weight of the usage composition.

1,1,1-Trichloro-2-methylpropan-2-ol, commonly known as chlorobutanol, with water solubility of about 0.8%; a typical effective level of chlorobutanol is from about
10 0.1% to about 0.5%, by weight of the usage composition.

4,4'- (Trimethylenedioxy)bis-(3-bromobenzamidine) diisethionate, or dibromopropamidine, with water solubility of about 50%; when dibromopropamidine is used as the preservative in the present invention it is typically present at a level of from about 0.0001% to about 0.05%, preferably from about 0.0005% to about 0.01% by weight
15 of the usage composition.

Mixtures of the preferred halogenated compounds can also be used as the preservative in the present invention.

(C). Cyclic Organic Nitrogen Compounds

Preferred water-soluble preservatives for use in the present invention are cyclic
20 organic nitrogen compounds. Some non-limiting examples of cyclic organic nitrogen compounds suitable for use in the present invention are:

(a) Imidazolidinedione Compounds

Preferred preservatives for use in the present invention are imidazolidione compounds. Some non-limiting examples of imidazolidinedione compounds suitable for
25 use in the present invention are:

1,3-bis(hydroxymethyl)-5,5-dimethyl-2,4-imidazolidinedione, commonly known as dimethyloldimethylhydantoin, or DMDM hydantoin, available as, e.g., Glydant® from Lonza. DMDM hydantoin has a water solubility of more than 50% in water, and is mainly effective on bacteria. When DMDM hydantoin is used, it is preferable that it be
30 used in combination with a broad spectrum preservative such as Kathon CG®, or formaldehyde. A preferred mixture is about a 95:5 DMDM hydantoin to 3-butyl-2-

iodopropynylcarbamate mixture, available under the trade name Glydant Plus[®] from Lonza. When Glydant Plus[®] is used as the preservative in the present invention, it is typically present at a level of from about 0.005% to about 0.2% by weight of the usage composition;

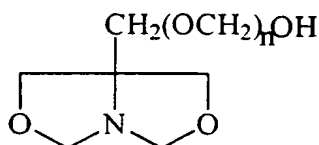
5 N-[1,3-bis(hydroxymethyl)2,5-dioxo-4-imidazolidinyl]-N,N'-bis(hydroxymethyl) urea, commonly known as diazolidinyl urea, available under the trade name Germall II[®] from Sutton Laboratories, Inc. (Sutton) can be used as the preservative in the present invention. When Germall II[®] is used as the preservative in the present invention, it is typically present at a level of from about 0.01% to about 0.1% by weight of the usage composition;

10 N,N''-methylenebis{N'-[1-(hydroxymethyl)-2,5-dioxo-4-imidazolidinyl]urea}, commonly known as imidazolidinyl urea, available, e.g., under the trade name Abiol[®] from 3V-Sigma, Unicide U-13[®] from Induchem, Germall 115[®] from (Sutton) can be used as the preservative in the present invention. When imidazolidinyl urea is used as the preservative, it is typically present at a level of from about 0.05% to about 0.2%, by weight of the usage composition.

Mixtures of the preferred imidazolidinedione compounds can also be used as the preservative in the present invention.

(b) Polymethoxy Bicyclic Oxazolidine

20 Another preferred water-soluble cyclic organic nitrogen preservative is polymethoxy bicyclic oxazolidine, having the general formula:



25 where n has a value of from about 0 to about 5, and is available under the trade name Nuosept[®] C from Hüls America. When Nuosept[®] C is used as the preservative, it is typically present at a level of from about 0.005% to about 0.1%, by weight of the usage composition.

Mixtures of the preferred cyclic organic nitrogen compounds can also be used as the preservative in the present invention.

(D). Low Molecular Weight Aldehydes

(a). Formaldehyde

5 A preferred preservative for use in the present invention is formaldehyde. Formaldehyde is a broad spectrum preservative which is normally available as formalin which is a 37% aqueous solution of formaldehyde. When formaldehyde is used as the preservative in the present invention, typical levels are from about 0.003% to about 0.2%, preferably from about 0.008% to about 0.1%, more preferably from about 0.01% to about
10 0.05%, by weight of the usage composition.

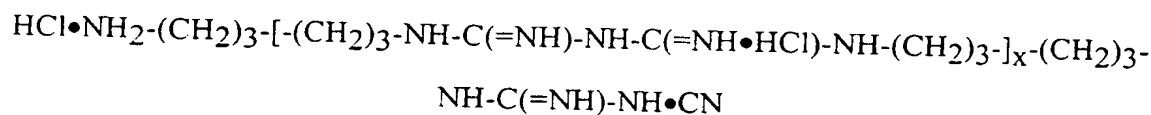
09856017 051601

(b) Glutaraldehyde

A preferred preservative for use in the present invention is glutaraldehyde. Glutaraldehyde is a water-soluble, broad spectrum preservative commonly available as a 25% or a 50% solution in water. When glutaraldehyde is used as the preservative in the present invention it is typically present at a level of from about 0.005% to about 0.1%, preferably from about 0.01% to about 0.05%, by weight of the usage composition.

(E). Quaternary Compounds

Preferred preservatives for use in the present invention are cationic and/or quaternary compounds. Such compounds include polyaminopropyl biguanide, also known as polyhexamethylene biguanide having the general formula:



Polyaminopropyl biguanide is a water-soluble, broad spectrum preservative which is available as a 20% aqueous solution available under the trade name Cosmocil CQ® from ICI Americas, Inc., or under the trade name Mikrokill® from Brooks, Inc.

1-(3-Chlorallyl) -3,5,7-triaza-1-azoniaadamantane chloride, available, e.g., under the trade name Dowicil 200 from Dow Chemical, is an effective quaternary ammonium preservative; it is freely soluble in water; however, it has the tendency to discolor (yellow), therefore it is not highly preferred.

Mixtures of the preferred quaternary ammonium compounds can also be used as the preservative in the present invention.

When quaternary ammonium compounds are used as the preservative in the present invention, they are typically present at a level of from about 0.005% to about 0.2%, preferably from about 0.01% to about 0.1%, by weight of the usage composition.

(F). Dehydroacetic Acid

A preferred preservative for use in the present invention is dehydroacetic acid. Dehydroacetic acid is a broad spectrum preservative preferably in the form of a sodium or a potassium salt so that it is water-soluble. This preservative acts more as a biostatic

09656047 "051601

preservative than a biocidal preservative. When dehydroacetic acid is used as the preservative it is typically used at a level of from about 0.005% to about 0.2%, preferably from about 0.008% to about 0.1%, more preferably from about 0.01% to about 0.05%, by weight of the usage composition.

5 **(G). Phenyl and Phenolic Compounds**

Some non-limiting examples of phenyl and phenolic compounds suitable for use in the present invention are:

4,4'-diamidino- α,ω -diphenoxypropane diisethionate, commonly known as propamidine isethionate, with water solubility of about 16%; and 4,4'-diamidino- α,ω -diphenoxyhexane diisethionate, commonly known as hexamidine isethionate. Typical effective level of these salts is about 0.0002% to about 0.05% by weight of the usage composition.

Other examples are benzyl alcohol, with a water solubility of about 4%; 2-phenylethanol, with a water solubility of about 2%; and 2-phenoxyethanol, with a water solubility of about 2.67%; typical effective level of these phenyl and phenoxy alcohol is from about 0.1% to about 0.5%, by weight of the usage composition.

15 **(H). Mixtures thereof**

The preservatives of the present invention can be used in mixtures in order to control a broad range of microorganisms.

20 Bacteriostatic effects can sometimes be obtained for aqueous compositions by adjusting the composition pH to an acid pH, e.g., less than about pH 4, preferably less than about pH 3, or a basic pH, e.g., greater than about 10, preferably greater than about 11. Low pH for microbial control is not a preferred approach in the present invention because the low pH can cause chemical degradation of the cyclodextrins. High pH for microbial control is also not preferred because at high pH's, e.g., greater than about 10, preferably greater than about 11, the cyclodextrins can be ionized and their ability to complex with organic materials is reduced. Therefore, aqueous compositions of the present invention should have a pH of from about 3 to about 10, preferably from about 4 to about 8, more preferably from about 4.5 to about 6. The pH is typically adjusted with inorganic molecules to minimize complexation with cyclodextrin.

30 **(9) Mixtures thereof**

II. ARTICLE OF MANUFACTURE

The composition of the present invention can also be used in an article of manufacture comprising said composition plus a spray dispenser. When the commercial embodiment of the article of manufacture is used, it is optional, but preferable, to include the preservative. Therefore, the most basic article of manufacture comprises uncomplexed cyclodextrin, a carrier, and a spray dispenser.

SPRAY DISPENSER

The article of manufacture herein comprises a spray dispenser. The cyclodextrin composition is placed into a spray dispenser in order to be distributed onto the fabric. Said spray dispenser is preferably any of the manually activated means for producing a spray of liquid droplets as is known in the art, e.g. trigger-type, pump-type, non-aerosol self-pressurized, and aerosol-type spray means. The spray dispenser herein does not normally include those that will substantially foam the clear, aqueous odor absorbing composition. It has been found that the performance is increased by providing smaller particle droplets. Desirably, the Sauter mean particle diameter is from about 10 μm to about 120 μm , more preferably, from about 20 μm to about 100 μm . Dewrinkling benefits are improved by providing small particles (droplets), as discussed hereinbefore, especially when the surfactant is present.

The spray dispenser can be an aerosol dispenser. Said aerosol dispenser comprises a container which can be constructed of any of the conventional materials employed in fabricating aerosol containers. The dispenser must be capable of withstanding internal pressure in the range of from about 20 to about 110 p.s.i.g., more preferably from about 20 to about 70 p.s.i.g. The one important requirement concerning the dispenser is that it be provided with a valve member which will permit the clear, aqueous odor absorbing composition contained in the dispenser to be dispensed in the form of a spray of very fine, or finely divided, particles or droplets. The aerosol dispenser utilizes a pressurized sealed container from which the clear, aqueous odor-absorbing composition is dispensed through a special actuator/valve assembly under pressure. The aerosol dispenser is pressurized by incorporating therein a gaseous component generally known as a propellant. Common aerosol propellants, e.g., gaseous hydrocarbons such as isobutane, and mixed halogenated hydrocarbons, which are not preferred. Halogenated hydrocarbon propellants such as

chlorofluoro hydrocarbons have been alleged to contribute to environmental problems. Hydrocarbon propellants can form complexes with the cyclodextrin molecules thereby reducing the availability of uncomplexed cyclodextrin molecules for odor absorption. Preferred propellants are compressed air, nitrogen, inert gases, carbon dioxide, etc. A more complete description of commercially available aerosol-spray dispensers appears in U.S. Pat. Nos.: 3,436,772, Stebbins, issued April 8, 1969; and 3,600,325, Kaufman et al., issued August 17, 1971; both of said references are incorporated herein by reference.

Preferably the spray dispenser can be a self-pressurized non-aerosol container having a convoluted liner and an elastomeric sleeve. Said self-pressurized dispenser comprises a liner/sleeve assembly containing a thin, flexible radially expandable convoluted plastic liner of from about 0.010 to about 0.020 inch thick, inside an essentially cylindrical elastomeric sleeve. The liner/sleeve is capable of holding a substantial quantity of odor-absorbing fluid product and of causing said product to be dispensed. A more complete description of self-pressurized spray dispensers can be found in U.S. Pat. Nos. 5,111,971, Winer, issued May 12, 1992, and 5,232,126, Winer, issued Aug. 3, 1993; both of said references are herein incorporated by reference. Another type of aerosol spray dispenser is one wherein a barrier separates the odor absorbing composition from the propellant (preferably compressed air or nitrogen), as disclosed in U.S. Pat. No. 4,260,110, issued April 7, 1981, and incorporated herein by reference. Such a dispenser is available from EP Spray Systems, East Hanover, New Jersey.

More preferably, the spray dispenser is a non-aerosol, manually activated, pump-spray dispenser. Said pump-spray dispenser comprises a container and a pump mechanism which securely screws or snaps onto the container. The container comprises a vessel for containing the aqueous odor-absorbing composition to be dispensed.

The pump mechanism comprises a pump chamber of substantially fixed volume, having an opening at the inner end thereof. Within the pump chamber is located a pump stem having a piston on the end thereof disposed for reciprocal motion in the pump chamber. The pump stem has a passageway there through with a dispensing outlet at the outer end of the passageway and an axial inlet port located inwardly thereof.

The container and the pump mechanism can be constructed of any conventional material employed in fabricating pump-spray dispensers, including, but not limited to: polyethylene; polypropylene; polyethyleneterephthalate; blends of polyethylene, vinyl acetate, and rubber elastomer. A preferred container is made of clear, e.g., polyethylene terephthalate. Other materials can include stainless steel. A more complete disclosure of commercially available dispensing devices appears in: U.S. Pat. Nos.: 4,895,279, Schultz, issued January 23, 1990; 4,735,347, Schultz et al., issued April 5, 1988; and 4,274,560, Carter, issued June 23, 1981; all of said references are herein incorporated by reference.

Most preferably, the spray dispenser is a manually activated trigger-spray dispenser. Said trigger-spray dispenser comprises a container and a trigger both of which can be constructed of any of the conventional material employed in fabricating trigger-spray dispensers, including, but not limited to: polyethylene; polypropylene; polyacetal; polycarbonate; polyethyleneterephthalate; polyvinyl chloride; polystyrene; blends of polyethylene, vinyl acetate, and rubber elastomer. Other materials can include stainless steel and glass. A preferred container is made of clear, e.g. polyethylene terephthalate. The trigger-spray dispenser does not incorporate a propellant gas into the odor-absorbing composition, and preferably it does not include those that will foam the odor-absorbing composition. The trigger-spray dispenser herein is typically one which acts upon a discrete amount of the odor-absorbing composition itself, typically by means of a piston or a collapsing bellows that displaces the composition through a nozzle to create a spray of thin liquid. Said trigger-spray dispenser typically comprises a pump chamber having either a piston or bellows which is movable through a limited stroke response to the trigger for varying the volume of said pump chamber. This pump chamber or bellows chamber collects and holds the product for dispensing. The trigger spray dispenser typically has an outlet check valve for blocking communication and flow of fluid through the nozzle and is responsive to the pressure inside the chamber. For the piston type trigger sprayers, as the trigger is compressed, it acts on the fluid in the chamber and the spring, increasing the pressure on the fluid. For the bellows spray dispenser, as the bellows is compressed, the pressure increases on the fluid. The increase in fluid pressure in either trigger spray dispenser acts to open the top outlet check valve. The top valve

allows the product to be forced through the swirl chamber and out the nozzle to form a discharge pattern. An adjustable nozzle cap can be used to vary the pattern of the fluid dispensed.

For the piston spray dispenser, as the trigger is released, the spring acts on the piston to return it to its original position. For the bellows spray dispenser, the bellows acts as the spring to return to its original position. This action causes a vacuum in the chamber. The responding fluid acts to close the outlet valve while opening the inlet valve drawing product up to the chamber from the reservoir.

A more complete disclosure of commercially available dispensing devices appears in U.S. Pat. Nos. 4,082,223, Nozawa, issued Apr. 4, 1978; 4,161, 288, McKinney, issued Jul. 17, 1985; 4,434,917, Saito et al., issued Mar. 6, 1984; and 4,819,835, Tasaki, issued Apr. 11, 1989; 5,303,867, Peterson, issued Apr. 19, 1994; all of said references are incorporated herein by reference.

A broad array of trigger sprayers or finger pump sprayers are suitable for use with the compositions of this invention. These are readily available from suppliers such as Calmar, Inc., City of Industry, California; CSI (Continental Sprayers, Inc.), St. Peters, Missouri; Berry Plastics Corp., Evansville, Indiana, a distributor of Guala[®] sprayers; or Seaquest Dispensing, Cary, Illinois.

The preferred trigger sprayers are the blue inserted Guala[®] sprayer, available from Berry Plastics Corp., or the Calmar TS800-1A[®], TS1300[®], and TS-800-2[®], available from Calmar Inc., because of the fine uniform spray characteristics, spray volume, and pattern size. More preferred are sprayers with precompression features and finer spray characteristics and even distribution, such as Yoshino sprayers from Japan. Any suitable bottle or container can be used with the trigger sprayer, the preferred bottle is a 17 fl-oz. bottle (about 500 ml) of good ergonomics similar in shape to the Cinch[®] bottle. It can be made of any materials such as high density polyethylene, polypropylene, polyvinyl chloride, polystyrene, polyethylene terephthalate, glass, or any other material that forms bottles. Preferably, it is made of high density polyethylene or clear polyethylene terephthalate.

For smaller fluid ounce sizes (such as 1 to 8 ounces), a finger pump can be used with canister or cylindrical bottle. The preferred pump for this application is the cylindrical Euromist II® from Seaquest Dispensing. More preferred are those with precompression features.

5

III. METHOD OF USE

The cyclodextrin solution, which contains the perfume and, optionally, e.g., surfactant and/or antimicrobial compound, etc., can be used by distributing, e.g., by placing the aqueous solution into a dispensing means, preferably a spray dispenser and spraying an effective amount onto the desired surface or article. An effective amount as defined herein means an amount sufficient to absorb odor to the point that it is not discernible by the human sense of smell yet not so much as to saturate or create a pool of liquid on said article or surface and so that when dry there is no visual deposit readily discernible. Distribution can be achieved by using a spray device, a roller, a pad, etc.

Preferably, the present invention does not encompass distributing the cyclodextrin solution on to shiny surfaces including, e.g., chrome, glass, smooth vinyl, leather, shiny plastic, shiny wood, etc. It is preferable not to distribute the cyclodextrin solution onto shiny surfaces because spotting and filming can more readily occur on the surfaces. Although the cyclodextrin solution can be used on human skin, care should be taken when an antimicrobial active is present in the composition.

The present invention encompasses the method of spraying an effective amount of cyclodextrin solution onto household surfaces. Preferably said household surfaces are selected from the group consisting of countertops, cabinets, walls, floors, bathroom surfaces and kitchen surfaces.

The present invention encompasses the method of spraying a mist of an effective amount of cyclodextrin solution onto fabric and/or fabric articles. Preferably, said fabric and/or fabric articles include, but are not limited to, clothes, curtains, drapes, upholstered furniture, carpeting, bed linens, bath linens, tablecloths, sleeping bags, tents, car interior, etc.

The present invention encompasses the method of spraying a mist of an effective amount of cyclodextrin solution onto and into shoes wherein said shoes are not sprayed to saturation.

The present invention encompasses the method of spraying a mist of an effective amount of cyclodextrin solution onto shower curtains.

The present invention relates to the method of spraying a mist of an effective amount of cyclodextrin solution onto and/or into garbage cans and/or recycling bins.

5 The present invention relates to the method of spraying a mist of an effective amount of cyclodextrin solution into the air to absorb malodor.

The present invention relates to the method of spraying a mist of an effective amount of cyclodextrin solution into and/or onto major household appliances including, but not limited to: refrigerators, freezers, washing machines, automatic dryers, ovens,
10 microwave ovens, dishwashers etc., to absorb malodor.

The present invention relates to the method of spraying a mist of an effective amount of cyclodextrin solution onto cat litter, pet bedding and/or pet houses to absorb malodor.

The present invention relates to the method of spraying a mist of an effective
15 amount of cyclodextrin solution onto household pets to absorb malodor.

The presence of the surfactant promotes spreading of the solution and the antimicrobial active provides improved odor control as well as antimicrobial action, by minimizing the formation of odors. Both the surfactant and the antimicrobial active provide improved performance and the mixture is especially good. When the
20 compositions are applied in the form of the very small particles, as disclosed hereinbefore, additional benefits are found, since the distribution is even further improved and overall performance is improved.

All percentages, ratios, and parts herein, in the Specification, Examples, and Claims are by weight and are approximations unless otherwise stated.

25 The following are non-limiting examples of the instant composition. Perfume compositions that are used herein are as follows:

PERFUME**A****PERFUME INGREDIENTS****Wt. %****4 - TERTIARY BUTYL CYCLOHEXYL ACETATE****5.00****BENZOPHENONE****3.00**

BENZYL SALICYLATE	5.00
CIS-3-HEXENYL SALICYLATE	1.20
CYMAL	5.00
DECYL ALDEHYDE	0.10
DIHYDRO MYRCENOL	2.00
DIMETHYL BENZYL CARBINYL ACETATE	0.50
FLOR ACETATE	3.00
FLORHYDRAL	0.40
GALAXOLIDE 50 DEP	15.00
HELIONAL	3.00
HEXYL CINNAMIC ALDEHYDE	10.00
LINALOOL	4.80
METHYL DIHYDRO JASMONATE	15.00
ORANGE TERPENES	1.20
LYRAL	25.00
UNDECYLENIC ALDEHYDE	0.50
VANILLIN	0.30
TOTAL	100.00

PERFUME	B	C
PERFUME INGREDIENTS	Wt. %	Wt. %
BETA GAMMA HEXENOL	0.35	0.00
CETALOX	0.05	0.05
CIS-3-HEXENYL SALICYLATE	2.70	1.00
CITRAL	0.35	0.00
CITRONELLAL NITRILE	2.00	2.50
CITRONELLOL	4.00	4.00
COUMARIN	0.70	0.70
DAMASCONE BETA	0.05	0.20
DECYL ALDEHYDE	0.50	0.35

09856047-054604

DIHYDRO MYRCENOL	0.70	2.00
FLOR ACETATE	7.00	7.00
FRUTENE	5.00	5.00
GALAXOLIDE 50 IPM	14.00	20.00
HELIONAL	2.00	2.00
HEXYL CINNAMIC ALDEHYDE	17.00	13.00
HEXYL SALICYLATE	3.00	0.00
MENTHOL	0.05	0.00
METHYL ANTHRANILATE	2.00	5.00
METHYL CEDRYLONE	5.00	5.00
METHYL DIHYDRO JASMONATE	3.50	5.00
METHYL DIOXOLAN	6.00	3.00
METHYL ISO BUTENYL	0.20	0.10
TETRAHYDRO PYRAN		
METHYL PHENYL CARBINYL	0.50	0.50
ACETATE		
ORANGE TERPENES	2.50	2.50
LYRAL	10.00	10.00
PARA HYDROXY PHENYL	2.00	1.00
BUTANONE		
PRENYL ACETATE	1.00	1.00
SANDALORE	0.20	1.20
TRIPLAL	0.20	0.50
UNDECALACTONE	4.00	4.00
VERDOX	3.45	3.40
Total	100.00	100.00

PERFUME**D**

PERFUME INGREDIENTS

Wt. %

ISO-E SUPER

5.00

AURANTIOL

1.00

09856017-051601

BENZYL SALICYLATE	14.65
CETALOX	0.20
CIS 3 HEXENYL ACETATE	0.50
CITRONELLOL	2.00
DIPHENYL OXIDE	0.70
ETHYL VANILLIN	0.40
EUGENOL	0.70
EXALTEX	1.20
FLOR ACETATE	2.30
GALAXOLIDE 50 DEP	9.00
GAMMA DECALACTONE	0.25
GERANIOL	2.50
GERANYL NITRILE	0.70
HEXYL CINNAMIC ALDEHYDE	10.00
INDOL	0.05
LINALOOL	5.00
LINALYL ACETATE	2.80
LRG 201	1.25
METHYL BETA-NAPHTHYL KETONE	1.90
METHYL CEDRYLONE	14.00
METHYL ISO BUTENYL TETRAHYDRO PYRAN	0.10
MUSK PLUS	6.00
ORANGE TERPENES	0.70
LYRAL	12.00
PATCHON	1.80
PHENYL ETHYL PHENYL ACETATE	1.00
SANDALORE	2.30
Total	100.00

PERFUME

E

PERFUME INGREDIENTS

Wt. %

09656017 054601

HEXYL CINNAMIC ALDEHYDE	12.65
ANISIC ALDEHYDE	0.55
BENZALDEHYDE	0.55
BENZYL SALICYLATE	10.00
BUTYL CINNAMIC ALDEHYDE	1.10
CIS 3 HEXENYL ACETATE	0.75
CIS-3-HEXENYL SALICYLATE	8.20
COUMARIN	3.25
DIHYDRO ISO JASMONATE	8.20
ETHYL-2-METHYL BUTYRATE	0.55
ETHYLENE BRASSYLATE	11.00
FRUCTONE	0.55
GALAXOLIDE 50 DEP	11.00
GAMMA DECALACTONE	4.35
HEXYL ACETATE	1.10
LINALOOL	10.00
AURANTIOL	2.15
NONALACTONE	1.10
TRIPLAL	0.30
UNDECALACTONE	11.00
UNDECAVERTOL	0.55
VANILLIN	1.10

TOTAL	100.00
-------	--------

PERFUME**F**

PERFUME INGREDIENTS	Wt. %
ISO-E SUPER	7.000
ALPHA DAMASCONONE	0.350
AURANTIOL	3.200
BETA NAPHTHOL METHYL ETHER	0.500

09356047-051604

CETALOX	0.250
CIS JASMONE	0.300
CIS-3-HEXENYL SALICYLATE	0.500
CITRONELLAL NITRILE	1.500
CITRONELLOL	1.600
COUMARIN	0.400
DIPHENYL OXIDE	0.150
ETHYL-2-METHYL BUTYRATE	0.010
EUCALYPTOL	0.650
EXALTOLIDE	0.500
FLOR ACETATE	2.000
FLORALOZONE	1.500
FLORHYDRAL	0.400
GALAXOLIDE 50 IPM	9.350
HEXYL CINNAMIC ALDEHYDE	7.000
HEXYL SALICYLATE	5.000
INTRELEVEN ALDEHYDE SP	0.450
IONONE GAMMA METHYL	4.150
LIGUSTRAL	0.600
LINALOOL	1.400
LINALYL ACETATE	1.400
LRG 201	0.400
LYMOLENE	1.000
METHYL ANTHRANILATE	2.250
METHYL BETA-NAPHTHYL KETONE	0.650
METHYL CEDRYLONE	5.000
METHYL ISO BUTENYL TETRAHYDRO PRYAN	0.200
ORANGE TERPENES	7.200
LYRAL	12.200
PHENOXANOL	6.950
PHENYL ETHYL ACETATE	0.350

09856017-051601
T09750-2109860

SANDALORE	1.940
TETRA HYDRO LINALOOL	4.200
TONALID	7.150
UNDECALACTONE	0.350
TOTAL	100.000

PERFUME**G**

PERFUME INGREDIENTS	Wt. %
MYRCENE	0.15
ORANGE TERPENES	1.25
DIHYDRO MYRCENOL	10.60
CYCLAL C	0.15
PHENYL ETHYL ALCOHOL	7.70
BENZYL ACETATE	0.10
NEROL	1.65
GERANIOL	1.75
METHYL ANTHRANILATE	0.95
VANILLIN	3.25
LYRAL	32.00
ISO E SUPER	12.40
LRG 201	6.50
HEXYL CINNAMIC ALDEHYDE	15.15
ethyl methyl phenyl glycidate	0.40
DIHYDRO ISO JASMONATE	5.00
METHYL CEDRYLONE	1.00
TOTAL	100.00

PERFUME**H**

PERFUME INGREDIENTS	Wt. %
BENZYL ACETATE	3.00
BENZYL SALICYLATE	20.00

09856017.054601

BETA GAMMA HEXENOL	0.10
CEDRAMBER	0.75
CETALOX	0.20
CIS JASMONE	0.20
CIS-3-HEXENYL SALICYLATE	1.50
COUMARIN	1.30
DAMASCENONE	0.10
DIHYDRO ISO JASMONATE	5.00
ETHYLENE BRASSYLATE	5.00
EXALTOLIDE	3.00
FRUCTONE	0.35
FRUTENE	2.00
GAMMA DECALACTONE	0.30
HEXYL CINNAMIC ALDEHYDE	12.50
HEXYL SALICYLATE	10.00
indol	0.10
ISO E SUPER	6.80
ISO EUGENOL	0.30
LACTOJASMON	0.10
LRG 201	0.50
METHYL ANTHRANILATE	1.00
METHYL DIHYDRO JASMONATE	6.00
ORANGE TERPENES	1.00
LYRAL	8.00
PARA CRESYL METHYL ETHER	0.20
PHENYL ETHYL ALCOHOL	2.00
SANDALORE	3.00
TRIMOFIX O	4.50
UNDECALACTONE	0.30
UNDECAVERTOL	0.30
VANILLIN	0.40

0956047-054604

VERDOX	0.20
TOTAL	100.00

The following are non-limiting examples of the instant composition. The following compositions are prepared by first making a clear premix containing ethanol, diethylene glycol, perfume, and Silwet L-7600 surfactant to insure that all perfume ingredients are pre-dissolved. In examples II, III, and IV, the stability aid, such as hydrophobic/hydrophilic copolymer, or vesicle forming agent, is added during the premix stage. In the main mix tank, hydroxypropyl beta cyclodextrin and 98% of the water are first mixed with moderate agitation for about 10 minutes. In the case of example I, this is followed by adding polyacrylate acid and Kathon with an additional 10 minutes of mixing. The clear premix is then added to the main mix slowly into the vortex with vigorous agitation for about 30 minutes so that a stable emulsion/dispersion is formed. pH trim with either HCl or NaOH and water hold are added last with final mixing under moderate conditions for about 30 minutes.

Examples	<u>I</u>	<u>II</u>	<u>III</u>	<u>IV</u>	<u>V</u>	<u>VI</u>
<u>Ingredients</u>	<u>Wt%</u>	<u>Wt%</u>	<u>Wt%</u>	<u>Wt%</u>	<u>Wt%</u>	<u>Wt%</u>
<u>Premix</u>						
Ethanol	3.0	3.0	3.0	3.0	5.0	5.0
Diethylene glycol	0.1	0.1	0.1	0.1	0.1	0.3
Perfume	0.1	0.1	0.1	0.1	0.1	0.1
Silwet L-7600	0.1	0.1	0.1	0.1	0.1	0.2
AA/TBA copolymer		0.1-0.5				
KRB			0.5			
Acrylates/acrylamide copolymer				0.1-0.5		
<u>Main Mix</u>						
HPBCD(a) or (b)	1.0	1.0	1.0	1.0	1.0	3.0

Sodium Polyacrylate	0.2					
(2500 M.W.)						
Bardac 2250 (quats)					0.15	
Kathon	3 ppm	3 ppm	3 ppm	3 ppm	3 ppm	3 ppm
HCl or NaOH	to pH 4	to pH 7	to pH 4	to pH 9	to pH 4	to pH 4
Distilled water	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.
Total	100	100	100	100	100	100

(a) Hydroxypropyl beta-cyclodextrin.

(b) Randomly methylated beta-cyclodextrin.

5 The compositions of the above Examples are sprayed onto clothing using, e.g., the TS-800 sprayer from Calmar, and allowed to evaporate off of the clothing.

Hydroxyethyl alpha-cyclodextrin and hydroxyethyl beta-cyclodextrin are obtained as a mixture from the hydroxyethylation reaction of a mixture of alpha-cyclodextrin and beta-cyclodextrin. They can be substituted for the HP-B-CD.

10 The compositions of the above Examples are sprayed onto clothing using a blue inserted Guala[®] trigger sprayer, available from Berry Plastics Corp. and a cylindrical Euromist II[®] pump sprayer available from Sequest Dispensing, respectively, and allowed to evaporate off of the clothing.

09656017 051604